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NBS Special Foreign Currency Program in Israel 1970-71

U.S.
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1972

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Special Foreign Currency Program in Israel 1970-71

H. Steffen Peiser and Max Klein

Office of International Relations
National Bureau of Standards
Washington, D.C. 20234



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U.S. DEPARTMENT OF COMMERCE, Peter G. Peterson, Secretary
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FOREWORD

The National Bureau of Standards PL 480 Foreign Currency Program in Israel is reviewed in this Publication. The purpose of this review is to allow interested scientists and scientific administrators to form opinions on the value and efficacy of such programs from a number of points of view, e. g., that of the grantor and grantee countries and that of a more general reader who might, for instance, be interested in examining an example of international cooperation and its possible success in fostering the general good of the two countries involved and of the international scientific community. The method of review used involves the presentation of a summary of each of the recent projects funded under this Program. In the summaries are included the project goals, some pertinent results and a list of publications which resulted from the specific support under this Program. Also included are the names of the NBS monitor and of the principal investigators. From the NBS viewpoint the Program is judged to have been productive. Appendices include the NBS program structures and pertinent excerpts from the enabling legislation. The purpose of these appendices is to indicate how the Program is imbedded in the overall NBS scientific program.

Lewis M. Branscomb
Director, National Bureau of Standards

ABSTRACT

An overview is given of grants awarded by the National Bureau of Standards under the Special Foreign Currency Program in Israel authorized by Public Law 480 and its amendments. Each grant is identified by title, principal investigator, institution in Israel, NBS monitor working in close technical touch with the project in Israel, and the monitor's organizational unit within NBS. The relevant work is then described briefly under the three headings "Summary of Description of Project Goals", "Results and Implications to Date" and "List of Publications that Resulted from the Project". To demonstrate the wide use of such grants over the entire Program Structure of NBS, the grant descriptions are ordered by the elements of that Program Structure. Editorial comment on the significance and purpose of the NBS/PL 480 grant program is confined to a Foreword and Introduction. The editors judge this grant program to have had a high benefit to cost ratio from the viewpoint of NBS.

Key words: Binational research cooperation; international scientific cooperation; Israel science and technology; physical science research administration; PL-480 Programs; research planning; scientific research abstracts.

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Edited by

H. Steffen Peiser and Max Klein

1. INTRODUCTION

Information on scientific research and technical innovation is published in specialized journals. A literature devoted to abstracts also has an important function when it is collected and ordered into scientific fields. The present publication, a collection of summaries of scientific research, has a purpose different from those associated with such conventional publications. We, the editors, are trying to assemble evidence on which a cooperative scientific program can be evaluated, we are not trying to inform scientists in specialized fields about recent scientific news. In particular, we are looking at the overall Special Foreign Currency Program of the National Bureau of Standards (known as the NBS/PL 480 Program) in Israel over roughly the past two years. We are here presenting not our own assessment of the program but are, rather, attempting to present sufficient information in a useful form for the Program to be evaluated by interested persons. In this connection, requests for more detailed additional information would always be welcome as would comments and criticisms of the Program. We are ourselves aware that certain features of the Program could be improved in the future.

The assessment of this Program is desirable because it is an unusual one. Such an assessment could well be done from a number of viewpoints; for instance, those of the grantor and grantee institutions as well as from those relating to the broad national goals of each country. The Program has already been carefully examined from the point of view of the NBS by NBS management and found to be of considerable assistance to that organization in carrying out its mission. It supplements the research output of the NBS and enhances international collaboration among its scientists. The Program may have other significance. It demonstrates a technique by which a smaller country can keep in touch with a larger country when both are highly developed scientifically; and, in some instances, it may offer the opportunity to develop a specialized competence in one of the two countries where previously such competence did not exist.

Staff members of NBS have reacted favorably to this Program. A number of NBS personnel have commented that their own individual PL 480 projects in Israel have been successful and relevant. They have very strongly encouraged us to present them with sufficient information to allow them to take a broader view of the Program so as to enable them to see it in its entirety. This is something they have had difficulty doing in the past. This Technical Note is a first attempt at presenting the requisite information for producing such an overview.

A person attempting an analysis and evaluation of this Program need not necessarily concern himself with administrative details. For those who are interested, the editors have included some background administrative and historical material in Appendix II. To carry out its responsibilities under the various Acts of Congress, by which U.S. federal agencies have had the opportunity to use certain excess foreign currencies in Israel for the pursuit of scientific research and technical development work, the National Bureau of Standards has adopted guidelines for its Program as also reprinted in Appendix II.

The reader examining the Program from the grantor country's point of view has the opportunity to judge whether it has extended the research output of NBS appreciably and, if so, in useful directions, and whether U.S. national goals were served. To make this task easier we have assembled the sections of this Technical Note into categories identified by the NBS Program Elements under which all NBS projects are classified. The list of these Program Elements appears in Appendix I.

The Israeli oriented reader, on the other hand, should ask whether new techniques really have been brought to Israel by these projects and whether techniques already in existence have been given the opportunity to develop. Questions should be raised, such as: Have new competences been built up and old ones strengthened or have scientific and technological talents been diverted from the real national goals of Israel towards the longer-range goals of the U.S.A.? Have neighboring fields been enriched in Israel by cross-fertilization; have applications in industry been sparked and has the Program helped to provide Israel with a broadly based infrastructure of science and technology?

Readers with more specific viewpoints will ask such questions as:

1. Were the projects in the fields familiar to you well executed?

2. Did the senior investigators demonstrate exceptional competence which could be of special service in the future?
3. Did the projects contribute to problems of known importance to science, technology or society?
4. Is there evidence that contact between US and Israeli scientists was intellectually stimulating and helpful perhaps in related work?
5. Does the program appear to have contributed to the right climate for scientific progress and technological innovation?
6. Did the program help to widen the horizons of scientists towards application of their expertise to urgent national needs?
7. Does this report suggest that bi-national programs of this type should be developed for mutual benefit?

This list of questions is certainly not exhaustive nor are their answers by any means obvious.

This Technical Note is addressed most particularly to scientifically trained science administrators. In it the editors have summarized approximately \$500,000 worth of funded research considered valuable enough by Israeli officials for them to have augmented it by other sources of support. Matching funds of approximately the same magnitude were provided by the Israel institutions as well as a smaller invisible support from NBS supported services.

There are a number of administrative details which we feel are directly responsible for much of the success of this program. First of all, the NBS monitor has been very strongly encouraged to carry on direct communication with the principal investigator. Secondly, proper design of visits by the NBS monitors to Israel has broadened the basis of interaction. Thus, it should be obvious that the quality of the input to the NBS/PL 480 Program from the NBS monitor can depend strongly on his knowledge of the general Israeli scientific context in which the particular project which he is monitoring is imbedded. For these reasons, whenever it becomes necessary, for scientific reasons, for an NBS monitor to visit his project in Israel, he is strongly urged to visit as many additional scientific institutions and laboratories as possible and to describe, in writing, on his return, his view of the scientific competences and the particular strengths and weaknesses which he

observed. In addition to serving to broaden the outlook of the particular NBS monitor making the visits, this increases the extent of the contacts between Israeli scientists and the NBS staff, thereby enabling the Israeli scientist to see the NBS from the various points of view brought by the NBS visitors. This increases the likelihood that Israeli scientists involved in the Program will, to a certain extent, insert an NBS point of view in addition to their own, into goals set for their NBS projects. By careful planning of such NBS staff visits their cost has been kept to around 2% of project funds available.

There are in the files of the Program a growing number of examples of collaborative work which has been of direct utility to either or both sides. Such collaborative efforts are extremely important in today's world. The unit for scientific research is generally no longer the individual scientist but rather the team. The complex and interdisciplinary nature of modern scientific work makes the use of self-contained, local expertise of much less utility by itself than as a component in collaborative efforts which cross lines normally separating institutions, countries and areas of research. In this regard, we wish to call attention by way of such an example to the report in this Technical Note concerning a project (page 66) which directly stimulated an experimental project within the NBS program in support of the Office of Saline Water, U.S. Department of Interior. The Israeli investigator also made a suggestion towards the solution of a serious problem the NBS monitor was having with the image-amplifying element in his field ion microscope. This suggestion was followed shortly after the Israeli investigator completed a visit to the NBS and resulted in the complete elimination of the problem - saving large expenditures of NBS time and money. This collaboration would not have taken place had there been no monitor-investigator relationship. However true these and other benefits from NBS collaboration with Israeli institutions may have been the Program as a whole must be judged on the scientific merits of the individual projects. It is for that reason that we have given more technical details than are normally submitted to science administrators. It is timely to look at this Program, because the PL 480 Program in Israel is phasing out. We feel that consideration for some new mechanism for continued cooperation between the NBS staff and Israeli science is in order, provided the evaluation of the results recorded in this Technical Note is favorable.

A.2. CALIBRATION TRANSFER SERVICE

A.2. Calibration Transfer Service

Project Title: DEVELOPMENT OF A POWER MEASUREMENT SYSTEM FOR AUDIO FREQUENCY WITH AN
ACCURACY OF 0.1%

Principal Investigator: Professor S. Stricker

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. R. S. Turgel

NBS Institute or Center and Division: Institute for Basic Standards
Electricity Division

Summary Description of Project Goals

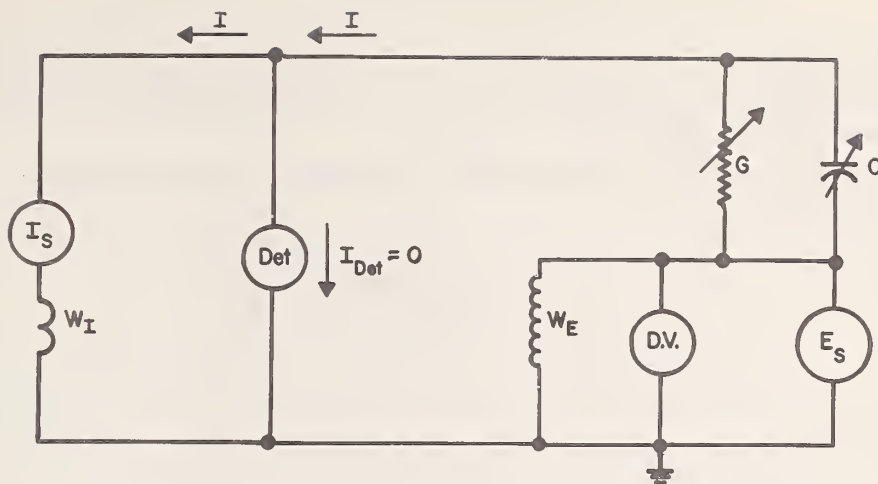
An attempt shall be made to build a solid state device for improved accuracy in the measurement of a-c average power at audio frequencies.

Results and Implications to Date

The endeavor to extend the range of power measurements to higher audio frequencies is an old one and during the last two decades substantial progress was made in this respect. Even today, however, the state of the art above 3000 Hz is uncertain.

In this project two innovative approaches were made to attain the prescribed aim. First a commercially available multiplier based on magneto-resistance effect of thin bismuth films mounted in a biased magnetic structure was used as a wattmeter. Non-linearities of the device and mutual inductance effects were partially compensated by appropriate circuitry. A prototype was built for a frequency range of 30 Hz to 4000 Hz and an estimated accuracy of 0.1% of full scale at power factor = 1.0 was obtained. It is believed that, by modification of the original components and suitable adaptation of the circuitry, frequency range and power factor range could be increased without reduction of the specified accuracy. A paper on this multiplier was submitted for publication in the proceedings of the EEMTIC conference to be held in Ottawa in June 1971.

The second approach was the development of a potentiometric circuit for the calibration of audio frequency wattmeters. This system relies on exact a-c voltage measurement using an ac-dc transfer voltmeter as developed at NBS by F. L. Hermach. It uses a network designed to shift the phase of a current proportional to the load current so that a null balance can be obtained. The power, P , is then calculated from the equivalent conductance of the network, G , and the measured ac voltage, E . When the deviations from ideal characteristics of the components are neglected the equation reduces the $P = E^2 G$.



- I_s Current Source
- E_s Voltage Source
- W_I Current coil of Wattmeter to be calibrated
- W_E Voltage " " " " " "
- Det Detector
- I Current through Wattmeter current coil
- D.V. Differential Voltmeter
- G Known variable Conductance
- C Known variable Capacitance

Fig. 1

The device was designed for a frequency range of 400 to 10,000 Hz. Therefore it does not permit a direct reference to d.c. It also has to be supplied with practically pure sinusoidal voltages and currents. The null-detector is a tuned one. All the components are easily built or obtainable for the given frequency range and accuracy.

Because of the complications of the compensating circuitry required, the magneto-resistance device does not lend itself as easily as the potentiometric system for use as a practical instrument. Accordingly, an instrument is being constructed based on the potentiometric system which, on completion, will be transferred to NBS. By means of this instrument, after establishing its calibration, the NBS capability for electric power measurement will be extended to higher audio frequencies.

List of Publications that Resulted from the Project

1. "Magnetoresistance Multiplier for the Accurate Measurement of Power in the Audio Frequency Range," S. Stricker, R. K. Even, S. Rogowski, EEMTIC proceedings to be published, Ottawa, June 1971.
2. "The Hall Effect and Its Applications," S. Stricker, Adv. in Electronics and Electron Physics, Vol. 25.

A.4. BENCHMARK DATA

Project Title: CALCULATIONS OF ATOMIC SPECTRA OF THE RARE-EARTHS

Principal Investigator: Dr. Z. B. Goldschmidt

Institution: The Hebrew University of Jerusalem

NBS Monitor: W. C. Martin

NBS Institute or Center and Division: Institute for Basic Standards
Optical Physics Division

Summary Description of Project Goals

This effort will be addressed toward (a) extension of various available energy matrices by adding the algebraic matrices of different kinds of effective interactions, (b) calculation of the theoretical matrices of the most important configurations appearing in the rare-earth spectra, (c) systematic study of the odd levels of the spectra of the transition elements, (d) improvement of theoretical interpretations and predictions by including effective interactions in the theoretical formulas, (e) classification and theoretical interpretation of the available materials on the spectra of rare-earths, and (f) theoretical predictions of rare-earth spectra.

The project is to have the following specific aims:

1. Extension of the theoretical interpretation of Ce I.
2. Completion of theoretical work on Gd I, Yb I, Eu I, La II, Ce II, Gd II, Yb II, Hf II, Pr III, Er IV.
3. Investigation of magnetic interactions in rare-earth spectra.

Results and Implications to Date

A. Rare Earths and Actinides

The most important result achieved under the current project was the theoretical interpretation of many rare-earth spectra, with special emphasis on the very complex first and second spectra. Configuration interaction in groups of overlapping configurations was treated in detail, resulting in a good understanding of the energy-level structure and in reliable and consistent information on internal and configuration-interaction parameters. The fit between calculated and observed levels was further improved through the inclusion in the energy matrices of effective interactions, which represent, to second order of perturbation theory, the electrostatic interaction with all distant configurations.

The stage has been reached where it is possible to make detailed predictions about the structure of the rare-earth spectra, even in those cases where the experimental material is very poor.

The main results obtained under the current project are:

1. Ce I

(a) The odd configurations $4f(5d+6s)^3 + 4f^2(5d+6s)6p + 4f5d6s7s$.

The algebraic matrices of this group of configurations have been constructed.

The theoretical interpretation of the three low configurations $4f(5d+6s)^3$ has

reached an advanced stage. The appropriate energy levels have been calculated, including configuration interaction and the two-electron 4f-5d effective interactions represented by the parameters E_1 and E_s . The fit obtained between calculated and observed levels is very good, the mean error Δ being 57 cm^{-1} . The calculations are being refined now, through the inclusion, in the energy matrices, of the complete set of two-electron 4f-5d effective parameters F_1 , F_3 , G_2 and G_4 , instead of E_1 and E_s .

The final results will be shortly published, as a counterpart to the paper entitled "Low Energy Level Structure of Neutral Cerium (Ce I) by William C. Martin of the N.B.S.

(b) The even configurations $4f^2(5d+6s)^2 + 4f^2 6s 7s + 4f(5d+6s)^2 6p$.

The algebraic matrices of these configurations have been constructed, through the use of a special computer program written for this purpose (see paragraph C below).

2. Eu I and Gd II (paragraphs 1d and 2c in the research program).

The theoretical interpretation of the $4f^7(8S) n \ell n' \ell'$ configurations of these spectra has been completed. In particular, for each such configuration the coupling scheme closest to the physical coupling has been determined. It has been shown that configuration interaction also affects the couplings within the configurations. The results obtained are summarized in the paper published in *Physica*.

3. Yb I (paragraph 1c in the research program).

The theoretical interpretation of the $4f^{14} 6s 6p + 4f^{13} 5d 6s^2 4f^{14} (6s^2 + 5d 6s + 6p^2 + 5d^2) + 4f^{13} (5d + 6s)^2 6p$ configurations has been completed. The results obtained are being prepared for publication.

4. Ce II (paragraph 2c in the research program).

The theoretical interpretation of the $4f^2(5d+6s) + 4f(5d+6s) 6p + (5d+6s)^3, 4f(5d+6s)^2, 4f^2 6p$ configurations has been completed. The results obtained are being prepared for publication.

5. Pr IV 4f5d, Ce II 4f5d, La II 4f5d, Yb III 4f¹³5d.

The effects of a complete two-electron 4f-5d effective interactions on the energy level structure of the above mentioned configurations were investigated. The inclusion of these interactions in the energy level calculations greatly improved the fit between calculated and observed levels. Numerical values were obtained for the radial parameters representing these interactions.

B. Magnetic Interactions

1. A systematic investigation was conducted of the effects of spin-spin, spin-other-orbit, and the mixed electrostatic spin-orbit effective interactions on the energy level schemes of ℓ^N configurations of heavy atoms. The inclusion of these interactions in the energy-level calculations greatly improved the fit between observed and calculated multiplet splittings. Reliable and consistent values of the appropriate parameters were determined, which agree remarkably well with available

theoretical predictions. Some of the results obtained are summarized in papers 2 and 5 in the list of publications.

2. Formulas were derived for the matrix elements of the magnetic interactions in configurations of the type $\ell^N \ell'$ comprising non-equivalent electrons. These have a particularly simple form for configurations comprising an electron and a hole.

C. Formulas and numerical values of the matrix elements.

The theoretical interpretation of complex spectra such as those of the rare-earths entails the construction of a great number of high order algebraic matrices. This involves a great amount of "tensor-algebraic" and arithmetic calculations. Several years ago computer programs were constructed, which receive as an input an algebraic formula for the matrix elements and give out the numerical values of these elements. The problem of the huge amount of arithmetic calculations was thereby solved, but the construction of the algebraic formulas still remained one of the tasks of the theoretical investigator.

Two manuscripts deal with this subject. In the first paper entitled "Electrostatic Interaction between Configurations Comprising Electrons and Holes" (No. 4 in the list of publications), new identities are derived, which enable the construction of closed formulas for the matrix elements of the electrostatic interaction between (two-particle) configurations comprising an electron and a hole. Relations between these matrix elements and those corresponding to two electron configurations are obtained. Formulas are given, in which the matrix elements of the electrostatic interaction between three-particle configurations are expressed as linear combinations of matrix elements between two-particle configurations.

In the second paper entitled "Generalised Rajnak-Wybourn Identity" (No. 3 in the list of publications) the representation of the electrostatic interaction by unit operators makes it possible to derive a general equation which provides many identities. The Rajnak-Wybourn identity is obtained as a special case.

Making use of the identities obtained in the second paper, a computer program was recently constructed, which calculates and checks both the algebraic formulas and the numerical values of the matrix elements of the electrostatic interaction between any two configurations. The only data serving as input to this program are the "names" of the two configurations.

List of Publications that Resulted from the Project

1. "Coupling Schemes in the $4f^7(8S) n\ell n'\ell'$ Configurations of Eu I and Gd II", Z. B. Goldschmidt and S. Nir, Physica, 51, 222 (1971).
2. "Magnetic and Effective Interactions in ℓ^N Configurations of Heavy Atoms", Z. B. Goldschmidt, Journal de Physique, Coll. C-4, Supp. 11-12, 31, 163 (1970).

3. "Generalised Racah-Wigner Identity", J. Math. Phys. 12, 1018 (1971).
4. "Electrostatic Interactions between Configurations Comprising Electrons and Holes", Z. B. Goldschmidt, Phys. Rev. A3, 1872 (1971).
5. "Spin-dependent Interactions in the $3d^N$ Configurations of the Third Spectra of the Iron Group", A. Pasternak and Z. B. Goldschmidt, accepted for publication in Phys. Rev. A (1972).
6. "Magnetic and Effective Interactions in ℓ^N Configurations of Heavy Atoms", Z.B. Goldschmidt, Colloque du C.N.R.S. on Theorie de la Structure Atomique, Page 18, July 1970.

A.5. STANDARD REFERENCE DATA

Project Title: COMPLEX STABILITY CONSTANTS

Principal Investigator: Professor Y. Marcus and Professor A. S. Kertes

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. H. J. White

NBS Institute or Center and Division: Office of Standard Reference Data

Summary Description of Project Goals

The purpose of this project is to collect, evaluate, and compile equilibrium data for complex formation equilibria in homogeneous and heterogeneous systems.

Results and Implications to Date

The project started in June 1968 with the aim of collecting, compiling and tabulating constants of complex formation equilibria in homogeneous and heterogeneous systems as obtained from solvent extraction distribution data.

This work is part of an international project carried out within the frame of the activities of the Commission on Equilibrium Data (Commission V6), Analytical Chemistry Division, International Union of Pure and Applied Chemistry (IUPAC). It was initiated at the Commission's meeting in Prague, August 1963, and a Task Group of four Commission members (Professors Dyrssen - Sweden; Freiser - USA; Kertes - Israel; and Marcus - Israel; Professor Stary - Czechoslovakia - replaced Professor Dyrssen in 1969) was set up to carry out the work. The principal investigators of the present NBS project have been charged with the compilation of data obtained by the following groups of extracting agents:

Organophosphorus Extractants

Phosphoric and pyrophosphoric acids

Phosphonic and phosphinic acids

Phosphates

Phosphonates and phosphinates

Phosphinic oxides

Compound-Forming Extractants

High-molecular weight carboxylic acids

Alkyl-naphthalene sulfonic acids

Solvating Extractants

Alcohols

Ethers

Ketones

Esters

Ion-Pair Forming Extractants

Alkylamines

Quaternary ammonium salts

Inert Solvent Extractants

Hydrocarbons

Chlorinated hydrocarbons

By the end of 1970 the collection and tabulation of complex constants with the organophosphorus extractants was completed. This work generated tables containing about 2000 entries extracted from over 400 scientific communications.

List of Publications that Resulted from the Project

Data compilation submitted to National Standard Reference Data System.

Project Title: THE SPECTROSCOPY OF TWO-ELECTRON ATOMS

Principal Investigator: C. L. Pekeris

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. W. C. Martin

NBS Institute or Center and Division: Office of Standard Reference Data

Summary Description of Project Goals

The aim of this project is to obtain very accurate solutions of the Schrodinger wave equation for 2-electron atoms, for the purpose of (1) determining theoretical term-values of all the observed singlet and triplet S-states for all the atoms, (2) determining theoretical term-values for all the singlet and triplet 2P, 3P, 4P and 5P states of two-electron atoms for $2 \leq Z \leq 10$, (3) evaluating accurate f-values for transitions between the above S and P states.

Results and Implications to Date

Dr. Pekeris, the principal investigator, reports that two papers are under preparation; their tentative abstracts are as follows:

Abstract 1:

Calculations have been made of the energy levels and other properties of the states n^1S , n^3S , n^1P and n^3P , $n = 2$ to 5, for atoms belonging to the helium isoelectronic sequence up to $Z = 10$, and also for the higher excited S states of helium. The theoretical term values, including the contributions from the masspolarisation correction and the relativistic effects of order α^2 , are listed in four tables. A detailed comparison with the experimentally determined energy differences between S and P states for He I up to F VIII shows a satisfactory agreement in almost every case, provided that we include an estimate of the Lamb-shift correction to the S state energy level when considering transitions involving the 1^1S , 2^1S or 2^3S states.

Abstract 2:

f-values have been computed for the transitions m^1S-n^1P , $m = 1$ to 5, $n = 2$ to 5 and m^3S-n^3P , $m, n = 2$ to 5 for members of the helium isoelectronic sequence up to $Z = 10$. The agreement between the results obtained using the dipole length and velocity formulae, together with the convergence of the results as an increasing number of terms are included in the expansions of the wave functions, indicate that the values obtained are accurate to within one percent or better for the large majority of the transitions.

In these papers, we were fortunate in having received preprints of papers by Professors Edlén, Löfstrand and Svensson. In these papers, we found very recent experimental measurements on the spectra of two-electron atoms, going up to neon. The agreement between the measured wavelengths and our theoretical values was very good. These wavelengths extended from the x-ray region of around 15 \AA out to the visible.

List of Publications that Resulted from the Project

1. "Fine-Structure of the 2^3p , 3^3p , and 4^3p States of Li^+ ", B. Schiff, Y. Accad and C. L. Pekeris, Phys. Rev. A1 1837 (1970).
2. "Low-Energy Photoionization for the 1^1S and 2^1S States of Helium", Verne Jacobs, Phys. Rev. A1 289 (1971).

Project Title: DESCRIPTION AND ANALYSIS OF THE SPECTRA OF NEUTRAL AND SINGLY-IONIZED
ERBIUM AND HOLMIUM

Principal Investigator: Dr. Nissan Spector

Institution: Israel Atomic Energy Commission - Soreq Nuclear Research Centre

NBS Monitor: Dr. W. C. Martin

NBS Institute or Center and Division: Office of Standard Reference Data

Summary Description of Project Goals

This project will involve: (1) Accurate measurements of wavelengths using mechanized comparators, (2) full description of rare-earth spectra by compilation of their line lists, using electronic computers, (3) spectrum analyses of atomic spectrum using electronic computers.

In the analysis of the spectra of these substances, stress will be put on measuring photographic plates, calculating new matrix elements, searching for energy levels and experimenting with various light sources.

Results and Implications to Date

Dr. Spector describes his results and the status of this project as follows:

During 1970, one of the major goals of this continuing contract was achieved: The full description of the erbium spectra in the photographic region in air was completed. Two separate lists, one of ErI and the other of ErII are available. The light emitted by three different sources (electrodeless discharge, sliding spark in helium and d.c. arc in air) was recorded on seven different spectrographs in five laboratories over a period of eight years. This resulted in a list of 5000 lines belonging to ErI and II. The work that was done in this laboratory was a participation in this common effort. The wavelength range covered is 2100A - 12300A. Full separation to ErI and ErII was achieved. The accuracy of the measurements - believed to range from 0.10 \AA^{-1} in the far U.V. to 0.01 \AA^{-1} in the I.R. - is compatible with the requirement of term analysis which is still needed in both spectra, and which is now in progress here.

Erbium thus becomes one of the few lanthanides to enjoy such an extensive description of its emission spectrum. The ensuing analysis is expected to bring about a full understanding of the energy level structure of both the neutral and singly ionized atom of erbium. It is needless to point out the significance of such an understanding to astrophysics, crystal structure, thermodynamic data for metals, and in particular, possible (though probably remote) uses in the laser industry of an emitting atom with such a density of levels and rich spectra.

In addition to the major work on erbium, work on other lanthanides was performed. Following an invitation by Prof. Jacquinet of C.N.R.S. to participate in the International Conference on the Theory of Atomic Spectra at Orsay, I presented recent calculations in singly ionized samarium and gadolinium and neutral terbium. The importance of working on a few lanthanides simultaneously was proved again when the extrapolated values of the f-d interactions gave energy level predictions in terbium which were quite different from the ones previously reported. The new values permitted a revision in the analysis of TbI and the location of new fundamental levels.

A theoretical achievement during 1970 is the calculation of the complete configuration $d^3d + d^7d$ (total possible levels: 168). This was done by active collaboration with the spectroscopy section of the Institute de Optica in Madrid, in particular with Dr. Olga Garcia Riquelme. Immediate application of the new calculations enabled us to interpret energy levels in the spectra of VII, NiIII, CoII and FeI and FeIII; and to show the linear behaviour of the new set of parameters; the 3d-4d electrostatic interactions in singly and doubly ionized atoms of the first transition period. In a forthcoming visit of Dr. Garcia Riquelme to our laboratory, this investigation will be continued.

Finally, active work is now in progress here on the coverage of the holmium spectra in the photographic infrared. This is done in collaboration with Dr. Jack Sugar of the NBS, Washington. We presently intend to compile a line list of HoI and HoII from 7300-1200 \AA , accurately measured and fully separated into I and II. Work on other wavelength regions will be performed at the NBS. The completion of the description of the holmium spectra and their subsequent analysis have the first priority under this contract. The international character of such a project is, thus, evident. Progress is being made in various laboratories in the world on subjects initiated or investigated here.

The NBS monitor has made the following evaluation:

Dr. Spector's work under this contract has recently yielded a large increase in the observed data.

1. He has covered the region between 2600 \AA - 3100 \AA in his spark exposures of erbium. This will enable him to proceed immediately with computer searches in both ErII and ErIII.
2. In collaboration with Dr. J. Sugar of NBS the DyIII spectrum was photographed and will now be measured and analyzed.
3. The observations of Ho in emission in the I.R. and in absorption in the visible and U.V. have been completed by Dr. Spector and Dr. Sugar. It is believed that a combination of the resulting line lists will provide the best way to begin the analysis of HoI.

The research has progressed well ahead of schedule and these data are now being prepared for computations.

List of Publications that Resulted from the Project

1. "New Description of the Gadolinium Spectra in the Photographic Infrared", Nissan Spector and S. Held, Astrophysical Journal, Vol. 159, See Page 1079 (1970).
2. "Classification of Solar Lines of Singly Ionized Gadolinium", Nissan Spector, Astrophysical Journal, Vol. 159, See Page 1091 (1970).
3. "Extension of the Analysis of Singly Ionized Gadolinium (GdII)", Nissan Spector, J. Opt. Soc. Am., 60 (1970).
4. "The Configurations $3d^24d$ and $3d^24f$ of Doubly Ionized Vanadium (VIII)", Nissan Spector, Optica Pura y Aplicada.
5. "Description of the Erbium Spectra in the Photographic Infrared", Nissan Spector and S. Held, Astrophysical Journal, 167, 193 (1971).
6. "New Low Levels of Singly Ionized Erbium (ErII)", Nissan Spector, Astrophysical Journal, 167, 205 (1971).
7. "Configuration Interaction in Singly Ionized Lanthanous (LaII)", Nissan Spector and U. Gotthell, Optica Pura y Aplicada, to be published.
8. "The 4f-5d Interactions in Singly Ionized Samarium and Gadolinium (SmII, GdII) and Neutral Terbium" Nissan Spector, Journal de Physique, Coll. C4 (4), 173 (1970).
9. "Transition from L-S to J-j in Singly Ionized Lanthanous", Nissan Spector, J. Optical Society of America, to be published.
10. "The $4f^{N-1} 6p6s^2$ Configuration in Neutral Gadolinium, Erbium and Ytterbium (GdI, ErI, YbI)", Nissan Spector, J. Optical Society of America, 61, 1350 (1971).
11. "The Energy Matrices of d^3d ", Nissan Spector and Olga Garcia Riquelme, Optica Pura y Aplicada, to be published.
12. "The 3d-4d Interactions in the Iron Group", Nissan Spector, Garcia Riquelme and Iglesias, Optica Pura y Aplicada, to be published.
13. "The $3d^8$ Configurations of Singly Ionized Nickel", Nissan Spector, NBS Journal of Res., to be published.

A.6. STANDARD REFERENCE MATERIALS PROGRAM

Project Title: TRACE ELEMENT ANALYSIS OF STANDARD REFERENCE MATERIALS

Principal Investigator: Saadia Amiel

Institution: Soreq Nuclear Research Center

NBS Monitor: Dr. P. D. LaFleur

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

The project will involve the characterization of certain materials within the NBS Standard Reference Materials Program. Included will be trace element analysis of several high purity Standard Reference Materials, including tin, refractory metals, botanical and biological materials. The techniques of delayed neutron and photonuclear counting will be utilized. X-ray techniques will also be used including x-ray spectrometry, x-rays induced by heavy ion bombardment, and x-ray fluorescence.

Results and Implications to Date

Dr. Amiel has submitted the following abstracts of two publications which are in preparation:

1.) S. Amiel and M. Mantel

APPLICATION OF HIGH RESOLUTION NON-DISPERSIVE
X-RAY SPECTROMETRY IN ACTIVATION ANALYSIS

Neutron activation of many nuclides results in the production of radioactive isotopes which on decay emit X-rays produced by electron capture, isomeric transitions, or internal conversion of their characteristic gamma rays.

These X-rays may be used to characterize the parent nuclide as well as to determine it quantitatively. This technique is applied to elements heavier than Na; X-rays emitted by elements having lower atomic numbers are too soft to be detected.

The use of solid state Si(Li) detectors having a resolution better than about a few hundred eV makes possible simultaneous determination, in the same sample, of elements having neighboring atomic numbers. The characteristics of this method are: (1) direct identification of the elements in question by accurate determination of the energy of their characteristic K or L X-rays (element assignment by gamma-ray spectrometry requires identification of gamma rays and determination of the corresponding half-lives, which may sometimes be ambiguous and elaborate); and (2) X-rays are representative of only thin samples, thus yielding supplementary information on homogeneity of sample composition.

A preliminary survey of the X-ray emission from neutron activated elements was performed with 15 elements. The Si(Li) detector employed

has a resolution of 315 eV (full width at half maximum) for the 6.4 keV X-ray of ^{57}Co and a geometry of 1 percent.

The sensitivity for X-ray assay of these elements was determined by irradiating thin samples in the pneumatic tube of the IRR-1 reactor. The results, as shown in the attached table, are expressed in dps/ μg at zero time after irradiation and normalized for five min. irradiation at a flux of 10^{13} n/cm² sec.

The following are preliminary data obtained

SENSITIVITIES OBTAINED BY NEUTRON ACTIVATION
FOLLOWED BY X-RAY SPECTROMETRY

| Element | Corresponding Isotope | t 1/2 | Sensitivity dps/ μg | Signal |
|-----------|-------------------------|--------|--------------------------------|-----------|
| Cobalt | ^{60}mCo | 10.5 m | $6 \cdot 10^3$ | Co X-rays |
| Copper | ^{64}Cu | 12.9 h | 7.10 | Cu X-rays |
| Zinc | ^{69}Zn | 14.0 h | 1.10 | Zn X-rays |
| Selenium | $^{79}\text{mSe}(85\%)$ | 3.9 m | $5 \cdot 10^3$ | Se X-rays |
| | $^{81}\text{mSe}(15\%)$ | 57 m | $5 \cdot 10^3$ | |
| Rubidium | ^{86}mRb | 1.0 m | $2 \cdot 10^3$ | Rb X-rays |
| Strontium | ^{87}mSr | 2.8 h | 1.10 | Sr X-rays |
| Niobium | ^{94}mNb | 6.3 m | $2 \cdot 10^3$ | Nb X-rays |
| Rhodium | ^{104}mRh | 4.4 m | $1 \cdot 10^5$ | Rh X-rays |
| Cadmium | ^{110}Cd | 49 m | 2.10 | Ag X-rays |
| Indium | ^{115}mIn | 4.4 h | $1 \cdot 10^2$ | In X-rays |
| Tin | ^{113}mSn | 20 m | $1 \cdot 10^{-1}$ | Sn X-rays |
| Iodine | ^{128}I | 25.0 m | $5 \cdot 10^2$ | Te X-rays |
| Caesium | ^{134}mCs | 2.9 h | $7 \cdot 10^2$ | Cs X-rays |
| Barium | ^{139}Ba | 87 m | $3 \cdot 10^{-1}$ | La X-rays |
| Cerium | ^{137}Ce | 9 h | $1 \cdot 10^{-2}$ | La X-rays |

2.) S. Amiel and M. Wiernik

SURFACE ANALYSIS BY MEASURING HEAVY-ION INDUCED X-RAYS

Induced X-rays are representative of the external layer of a sample, due to their short range. X-rays may be induced either by photons (X-ray fluorescence) or by charged particles. A special feature in analysis using charged particles is the possibility of focusing the beam, thus permitting the analysis of very small areas. When electrons are used for excitation, low energy X-rays of interest may not be detected due to the

interference of the bremsstrahlung radiation produced. This effect disappears when heavier ions are used.

X-ray spectrometry using heavy ions, which have a very low penetrating power, may thus provide information on the elemental composition of the extreme outer layer of a sample. In addition, by varying the energy of the incident beam and looking for the appearance of the characteristic X-rays of the substratum, the thickness of very thin films (several atomic layers) can be measured.⁽¹⁾ The combination of both techniques may provide a useful tool for bremsstrahlung-free chemical analysis at variable depth; this may be quite useful in studies of surfaces with regard to homogeneity, diffusion, fractionation, etc., and may be of great importance in the characterization of high purity reference materials.

Preliminary experiments were carried out with a Texas Nuclear neutron generator which was modified for use as a heavy ion accelerator ($E \leq 150$ kV), and connected to a specially constructed vacuum chamber which holds up to twelve samples and four radioactive sources for X-ray energy calibration.⁽²⁾ The X-rays induced in the samples were measured by a gas flow proportional counter or by a Si(Li) detector.

These experiments were performed by exposing samples of pure metals to ~ 1 μ A beams of several noble gases (Ar, Kr and Xe). Figure 1^(*) shows some of the results observed with the present equipment⁽³⁾.

Experiments to obtain quantitative results for sensitivities, ion mass effects, X-rays induced in the projectiles upon collision, and other experimental parameters of analytical significance are in progress.

(*) Not reproduced in this Technical Note.

References

1. W. P. Saylor and C. L. Marks, Private Communication.
2. R. Herman, S. Saviano, and M. Wiernik, Israel AEC Annual Report (1970).
3. S. Amiel and M. Wiernik, Israel AEC Annual Report (1970).

A number of possible applications have been discussed for the techniques developed. Dr. Amiel describes some of these and gives an overall view of the project as follows:

Matrices in which the NBS expressed special interest, and which our group are prepared to study, include botanical samples (such as homogenized dry leaves of various plants, e.g. pear, tomato, citrus, alfalfa, pine needle etc. as well as wood pulp) and biological samples (such as blood serum and liver tissue). These samples have to be analysed for about 12 principle elements, and some of the samples for as many elements as possible, down to the parts per billion (ppb) range. Other types of samples will include seaweeds which may be of importance in oceanography (e.g., for variations in composition which may have implications regarding exploration for food and minerals in the oceans).

Since a major part of the program will deal with organic samples where an accurate picture of the composition with regard to minor and trace constituents is needed, it is proposed to study possible losses of certain elements upon neutron irradiation which may result in volatile species being formed containing the activities of interest and thus affect the accuracy and precision of the assay.

Various standard glasses and alloys were also mentioned as possible samples of interest to the NBS and could be studied by mutual arrangement.

Techniques to be applied for analysis will be mainly nuclear ones, with the major focus on activation analysis, using γ ray spectrometry (with Ge-Li and NaI spectrometers) neutron counting (both delayed neutrons and photoneutrons) radiochemical processing and β assay. Use or preparation of suitable computer program for data processing will also be made. Techniques such as atomic absorption spectrophotometry (e.g., using the solid-mix technique to avoid dissolution), gas chromatography, X-ray fluorescence as well as other methods will be used separately and in combination to attain the necessary requirements and specifications.

New methods and modifications of existing ones will be investigated to improve the results obtainable and new procedures aimed at meeting the requirements of trace element assay of complex matrices will be investigated. The use of short irradiations with the aid of a shuttle rabbit at the reactor and assay of very short lived isomers and isotopes will be further investigated, after the preliminary stage was found very promising.

Parallel to the main avenue of the program, as mentioned above, an attempt will be made to explore the analytical feasibility, for the purpose of the Standard Reference Materials program, of X-ray spectrometry utilizing three techniques:

- (1) X-ray spectrometry of radioactivated samples, where X-rays result either from electron capture decay, or upon isomeric transition and conversion of low energy gamma rays present in the decay of neutron irradiated samples.
- (2) X-rays induced by heavy ion bombardment.
- (3) X-ray fluorescence using radioactive sources.

The specificity of X-ray counting and spectrometry lies in their very short range, thus permitting analysis of thin samples and foils; but greater significance lies especially in the ability to analyze by these techniques the composition of surfaces, and to follow surface phenomena of aging, e.g. migration and fractionation upon diffusion or corrosion. Results may then be compared to the gross sample composition, e.g. using γ ray spectrometry. This may be of interest in metallurgy where homogeneity of alloys is referred to the entire bulk (or from center to half top, and not to the surface). The use of heavy ions for X-ray induction has a great advantage due to the very low penetration of the ions at energies of 40 to 100 KV (several atomic layers) and very low bremsstrahlung. This facilitates the observation of variations in composition and contamination at a depth up to several atomic layers ($< 1 \mu\text{g}/\text{cm}^2$). The availability of silicon detectors with resolutions much better than the separation in KX-ray energies between neighboring elements makes X-ray spectrometry very attractive for multi-element assay using either one of the X-ray emission methods mentioned above. Moreover, as resolutions become better than 200 eV, and the peak position

can be determined with precisions within several eV, one should seek for chemical effects due to various chemical combinations which may be visualized through shifts in the peak positions. This possibility may introduce another dimension, viz. the chemical state, into the analysis and will also be explored in the course of the project.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

Project Title: TRACE ANALYSIS BY ANODIC STRIPPING VOLTAMMETRY

Principal Investigator: Dr. Magda Ariel

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. John K. Taylor

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

This project is a study of the application of anodic stripping voltammetry to media containing varying proportions of organic solvents, including the problems posed by adsorption, solution and the effect of the medium on oxidation and reduction potentials; the extension of anodic stripping methods to solid electrodes, the formation of insoluble reduction oxidation products on the working electrode, applications to the solution of complex analytical problems.

Results and Implications to Date

In the course of this work, undertaken to further the exploitation of the analytical potential of stripping voltammetry, two new tools have been developed:

- (a) the rotated, nickel based, mercury film electrode (MFE) and
- (b) the Flow Cell.

The MFE has been investigated and its behavior compared to the prevalent Hanging Drop Mercury Electrode (HMDE) from both theoretical and practical points of view, including discussion of those points where the MFE diverges in practice from theoretical behavior. Among the numerous experimental parameters examined, the most important were: (a) the deposition of the mercury film, its thickness, uniformity, stability, criteria of malfunction etc. Stated succinctly: the MFE shows improved sensitivity, better resolution of adjacent current peaks and, due to its ruggedness, is preferable whenever the analytical procedure requires vigorous solution stirring or electrode transfer (Medium Exchange without Flow Cell): on the other hand, it has a relatively higher residual current than the HMDE, a narrower useful potential range and a limited lifetime, often shortened further by the presence of seemingly innocuous solutes. Best results are obtained with the mercury film deposited on a nickel substrate; complete details of construction, coating, operation and applications to the analysis of complex samples were reported.

Intermetallic compounds formed in the mercury (amalgam) phase, either between the mercury and other metals or between metals dissolved in it, have been discussed. This phenomenon, first encountered in stripping voltammetry with mercury drop electrodes suspended from metal (Pt, Au, etc.) wires, and usually regarded as an interference, may be exploited for trace analysis; the depression of the zinc stripping current by platinum has been shown to provide a sensitive means for the estimation of traces of Pt^{+4} in solution (10^{-7}M and less - e.g. the zinc stripping current obtained, under certain, defined conditions with a 8 ppb Zn^{+2} solution, is decreased by 10% by the presence of 4 ppb Pt^{+4}).

A linear correlation between this depression effect and Pt^{+4} concentration provides the basis for the latter's quantitative estimation.

The choice of supporting electrolyte from which pre-electrolysis is carried out is often dictated by the composition of the sample and is unsuited to the subsequent stripping step for one or more of the following reasons: unsatisfactory resolution, interferences present in relatively high concentrations, highly sloped base current, etc. The situation may be improved by effecting a Medium Exchange, i.e. transferring the electrode into a more suitable electrolyte before the stripping step. The Flow Cell developed in the present work permits this transfer to be effected without either breaking the electrical circuit or exposing the electrode to the atmosphere, thus preventing losses hitherto connected with this step; metals such as zinc, which could not be determined by Medium Exchange are now easily determinable.

The usefulness of the Flow Cell has been demonstrated through a series of determinations of trace amounts of lead and copper carried out in a number of standard steel samples. These analyses are characterized by the ease and speed of the procedure involved: due to the Flow Cell, analysis is carried out directly on the sample solution, without recourse to preliminary separation steps. Contamination risks are reduced considerably.

The Flow Cell has also been combined with an ion-exchange chromatographic column to provide an anodic stripping analogue of "chromatopolarography". This combination constitutes a convenient and sensitive means for obtaining elution curves, and for investigating and optimizing elution parameters.

The Flow Cell may also serve as the monitoring part of a continuous analytical system, with the appropriate electrode choice, according to the analyte involved; due to its construction, the Cell lends itself to convenient intermittent standardization, by simply diverting the flow from the analyte to the standardizing solution.

The complex samples analysed by anodic stripping voltammetry included: (a) zinc in silicates and rocks; (b) trace metals (Zn, Pb, In, Cd, Cu) in standard glasses; (c) copper and lead in standard steels. The procedure developed for zinc in silicates, described and discussed in detail, served to illustrate the careful and considered technique required for successful trace analysis.

The controlled purity of the reagents and especially of the water employed was essential to the success of the project; an effective purification system for distilled water was described in detail.

Sensitive and selective trace determinations in complex samples can be effected by stripping voltammetry combined with the judicious use of these tools.

"IN SITU" MONITORING OF ORGANIC ELECTRODE PROCESSES BY THE TECHNIQUE OF INTERNAL REFLECTION SPECTROSCOPY (IRS)

This new project, directed at evaluating the potentialities of combined voltammetry and IRS at optically transparent electrodes as a source of data concerning organic electrode reactions, has gotten off to a good start. Results to date include:

Design of a suitable electro-optical cell,
methodology for preparing the semi-transparent electrodes,
investigation of potential distribution on the electrode as related to cell geometry,

investigation of absorbance changes in metal film due to potential modulation, and investigation of parameters affecting film "life-time" and stability.

The Internal Reflection technique applied in this work permits spectrophotometric observation of a region extremely close to the surface of a transparent electrode during an electrochemical process.

The main part of the cell used is the transparent electrode. Three types of electrodes were used: gold film electrodes produced by vacuum evaporation technique (with Bi_2O_3 as intermediate layer), platinum film electrodes evaporated directly on glass from a tungsten wire, and a gold film commercial electrode.

Two types of phenomena specific for the thin film electrodes were investigated in order to understand the behavior of this experimental system: (a) IR drop in the film; (b) absorbance changes in the absence of any absorbing species and/or any faradaic process.

(a) The "reversible" system $[\text{Fe(II)} \rightleftharpoons \text{Fe(III)} \text{ dimethylorthophenanthroline complexes}]$ was used as a model for measuring the extent of potential inhomogeneity on the electrode surface.

It could be shown experimentally, by measuring the potential changes at maximum distance on the film from the controlled point, that for millimolar solutions the current densities resulting at 20-50 mv/sec scans do not cause severe distortion of equipotential conditions. For 10 mM solutions it was proved advisable to use only narrow strips of the film to avoid considerable iR drops even at low rates of potential scanning.

The deterioration rate of the film proved to be very sensitive to high current densities. It was shown that the deterioration is gradual and is severest near the electrical connections to the film. This gradual corrosion of the film causes a gradual increase in the extent of the iR drop in the film during its "lifetime". In the subsequent development of any analytical method, this will have to be taken into account and checked by frequency "standard" runs with well defined systems.

(b) Absorbance changes of the internal reflected beam due to a modulated potential of the film electrode were monitored at both types of the gold electrodes used. In both cases the amplitudes and signs of the changes could be related to the spectrum of the metallic film (which was different for each type). It could be proved that the effect of the applied potential is the modulation of the energy level of the free electrons in the film, causing a shift in the optical parameters of the film, and resulting in a shift of several nm in the spectrum obtained.

Similar measurements at Pt electrodes, will be summarised in our next report. Further work underway includes:

- use of the Cell to follow the electrochemical oxidation reaction of a few suitable model compounds;
- evaluation of the effect of electrosorption;
- extension of the technique to the IR range, using Pt coated Ge plates.

List of Publications that Resulted from the Project

1. G. Koster, A. Golko and M. Ariel, Anodic stripping from a mercury film electrode, Israel

- J. Chem., 6 (1968), 38p.
2. G. Koster and M. Ariel, Analytical applications of the mercury coated rotating platinum electrode (MCRPE). Israel J. Chem., 7 (1969), 76p.
 3. M. Ariel, U. Eisner and S. Gottesfeld, Trace analysis by anodic stripping voltammetry II. The method of medium exchange, J. Electroanal. Chem., 7 (1964) p.307-314.
 4. G. Koster and M. Ariel, to be published.
 5. G. Koster, U. Eisner and M. Ariel, Trace analysis by anodic stripping voltammetry. V. Trace metal determination in silicate. 1. General considerations; the determination of zinc. Z. Anal. Chem., 224 (1967) 269-276.
 6. NBS Technical Note 505, Microanalytical Analysis Section: Summary of activities from July 1968 to June 1969, Washington. p.116.
 7. S. Gottesfeld and M. Ariel, Observation of electrode solution interface during electrochemical oxidations, Israel J. Chem., 7 (1969), 76p.

A.6. Standard Reference Materials Program

Project Title: PRODUCTION AND SUPPLY OF METAL OXIDE STANDARD REFERENCE MATERIALS BY THERMAL DECOMPOSITION OF CHLORIDE SALTS IN A SPRAY REACTOR

Principal Investigator: Dr. Eliahu Foa

Institution: Israel Atomic Energy Commission

NBS Monitor: J. L. Hague

NBS Institute or Center and Division: Institute for Materials Research
Office of Standard Reference Materials

Summary Description of Project Goals

The project will involve the production and supply of a number of Standard Reference materials by a technique based on chemical reactions occurring in small droplets at various temperatures, up to 1000°C. The reactions, involving the decomposition of chloride salts, will be conducted in the presence of gases such as argon, oxygen, hydrogen, ammonia, etc., thus producing very homogeneous final products. The technique developed thus far has been on a laboratory scale, but it is proposed to extend the scale so that larger quantities will be supplied for use as Standard Reference Materials.

The compounds of major interest at the present time are Al_2O_3 , ZrO_2 and MgO , but it is expected that the work can be extended to include such materials as ZnO , NiO , etc.

Results and Implications to Date

The work funded by NBS is part of a long-range project on reactions in sprays. The spray technique is particularly suitable for such reactions (solid-gas or liquid-gas) in which diffusion e.g. through a hard crust formed during the reaction, becomes rate-determining. In such cases a situation often develops where the reaction stops entirely at a certain stage because reactants cannot meet and/or products cannot diffuse away at a sufficient rate.

According to the basic invention made by an Israeli scientist, the late Dr. Aman, one of the reactants is broken up into fine droplets (a few hundreds of micron diameter) whereby a large specific surface is formed. More than 20 industrial Aman-reactors, mainly for the recovery of hydrochloric acid from steel pickle liquor, are operating successfully in several countries. In Israel a plant for the production of magnesium oxide from the chloride is planned.

The work under Contract NBS (G)-84 was intended for the production and supply of pure metal oxides by thermal decomposition of salts in a spray reactor, but the contribution could reach much wider goals.

1. On the one hand, equipment was developed which may be used as a prototype for future development of similar chemical reactors able to produce, by using the thermal dissociation technique in reactions in spray, chemical products of considerable purity in industrial quantities.
2. On the other hand, additional equipment was developed for the study of the reaction mechanism of thermal dissociation reactions in falling drops. This study will, hopefully, supply useful technical data for the construction of reactors of the type

mentioned in sub (1), and also for industrial reactors, particularly on the influence of the following variables on the thermodynamics of the dissociation reaction and on the possibility of controlling the characteristics of the reaction products. The variables are:-

- Temperature;
- Volume of the drops;
- Concentration of the salt solution;
- Contact time of the drop with the hot gases;
- Kind of gas;
- Rate of gas flow.

The possible applications of the work are of industrial importance in those cases where metal oxide, and perhaps other chemical products are required in conditions of high purity and in fine particles of well defined dimensions.

Present and future plans consist of the continuation of the work in the two fields already developed. The first involves the production of kilogram size batches of pure MgO to be used for production of pure crystals and the study of chemical reactions between potassium salts and phosphoric acid; the second, the improvement of the equipment mentioned in subparagraph (2) above; and detailed studies of the thermal dissociation reaction mechanism of many salts solutions.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

Project Title: SPECTROCHEMICAL ANALYSIS OF COMPONENTS OF INTEREST IN STANDARD REFERENCE MATERIALS

Principal Investigator: Dr. Sima Held

Institution: Soreq Nuclear Research Center

NBS Monitor: B. F. Scribner

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

This project will involve: (a) spectrochemical trace analyses for components of interest in SRM's for simulated lunar glasses and botanical materials; (b) spectrochemical trace analyses for components of interest in other SRM's as suggested by the National Bureau of Standards

Results and Implications to Date

Alfalfa is one of the botanical materials required by the U.S. National Bureau of Standards to serve as a standard reference material.

Dry citrus leaves, checked for the absence of Pb, were used as a matrix for the standards. A 1 mg Pb/ml stock solution was prepared by dissolving spectroscopically pure PbO (Johnson, Matthey) in dilute HNO₃ (analytical grade, Baker). The Sn solution which served as an internal standard was prepared by dissolving specpure SnO₂ (Johnson, Matthey) in H₂SO₄ (analytical grade, Merck). Standards in the concentration range 2-100, µg Pb per gram of leaf weight were prepared by saturating the citrus leaves with the requisite amounts of Pb in solution. Sn was added to a concentration of 50, µg Sn/g leaf weight.

The sample and standards were dried under an infrared lamp, ground in an agate mortar and excited under the conditions outlined in Table I. Transmittance was measured using a Jarrel Ash (non-recording) microphotometer. The photographic emulsion was calibrated with a seven step filter in the region of the analytical lines. Percentage transmittance was converted to Seidel-function values. Background corrections were applied.

The analytical curve used for the Pb determinations is based on the photometric measurements shown in Table II. The measurements were taken from three plates, for two series of independently prepared standards. The values of Pb in alfalfa given in Table III are based on measurements taken from five plates. The accuracy of the results was tested by adding a known amount of Pb to the alfalfa and checking the difference produced. The results of the recovery test are given in Table IV. This Table presents the results of determinations made of lead after known amounts of Pb were added to the alfalfa sample.

From Table III the lead in the alfalfa was found to be 5.5 $\mu\text{g/g}$. The additions were 2.5 and 10.0; accordingly, the lead would be predicted to be 8.0 and 15.5 as compared to 8.0 and 16.0 "found" (Table IV). This demonstrates a satisfactory recovery.

TABLE I

Experimental conditions for Pb determinations

| | | | | |
|----------------------|---|----------|-----|-----------|
| Spectrograph | Jarrel Ash Grating Spectrograph, Ebert mounting, 3.4m focal distance, grating 15000 grooves/inch, first order Step filter placed on the face of the slit. | | | |
| Analytical lines | PbI | 2833.06A | SnI | 2863.33 A |
| Slit width | 10 μ | | | |
| Mode of illumination | Image of the source on the collimator mirror | | | |
| Source | DC arc, 7 amp. Jarrel Ash Standard Varisource | | | |
| Analytical gap | 3 mm | | | |
| Electrodes | Graphite rods, Spectro-tech., Ultra Carbon Corp. Upper: pointed, 3 mm diam. Lower: 6 mm diam. with a hole 3 mm deep and wall thickness 0.7 mm | | | |
| Electrode charge | 14 mg | | | |
| Exposure time | 30 sec | | | |
| Emulsion | Eastman SA-1 | | | |
| Developing | D-19, 20°C, 5 min | | | |

TABLE II

Results of the photometric measurements

| Standards μg Pb/g leaves | n | $\overline{\Delta Y}$ | $S_{\Delta Y}$ | $\overline{S}_{\Delta Y}$ |
|-----------------------------|---|-----------------------|----------------|---------------------------|
| 2.5 | 4 | -0.92 | 0.061 | 0.030 |
| 5.0 | 4 | -0.65 | 0.055 | 0.027 |
| 10.0 | 5 | -0.42 | 0.031 | 0.014 |
| 20.0 | 5 | -0.17 | 0.063 | 0.030 |
| 25.0 | 6 | -0.07 | 0.042 | 0.019 |
| 50.0 | 5 | 0.19 | 0.071 | 0.032 |
| 100.0 | 2 | 0.42 | - | - |

n = number of measurements

$\overline{\Delta Y}$ = mean value of the log of the intensity ratio of the analytical lines

$$S_{\Delta Y} = \sqrt{\frac{\sum (\Delta Y - \overline{\Delta Y})^2}{n-1}}$$

$$\overline{S}_{\Delta Y} = \frac{S_{\Delta Y}}{\sqrt{n}}$$

TABLE III

Results of Pb determinations in alfalfa

| n | $\overline{\Delta Y}$ | $S_{\Delta Y}$ | $\overline{S}_{\Delta Y}$ | C μg/g | $\frac{S_c}{c}\%$ | $\frac{\overline{S}_c}{c}\%$ | Confidence interval μg/g |
|----|-----------------------|----------------|---------------------------|-----------|-------------------|------------------------------|--------------------------------|
| 11 | -0.61 | 0.044 | 0.013 | 5.5 | 13 | 4 | 5.0-6.0 |

$$\frac{S_c}{c} = 2.3 \left(\frac{1}{b} S_{\Delta Y} \right)$$

Confidence interval $\mu = \overline{c} \pm t \frac{\overline{S}_c}{c}$; t is taken from Tables of Student's t-distribution for the 95% probability level

TABLE IV

Results of recovery test

| Pb added to alfalfa $\mu\text{g/g}$ | n | Pb found $\mu\text{g/g}$ |
|---|---|-----------------------------|
| 2.5 | 5 | 8.0 |
| 10.0 | 6 | 16.0 |

Project Title: APATITES OF DIVALENT EUROPIUM

Principal Investigator: Dr. I. Mayer

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. Robert S. Roth

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

The research will include: 1) The preparation of $\text{Eu}_5(\text{XO}_4)_3\text{Y}$ type compounds, where $(\text{XO}_4)^{3-}$ is PO_4^{3-} , AsO_4^{3-} , VO_4^{3-} and MnO_4^{3-} and Y^- is F^- , Cl^- , Br^- and OH^- . 2) Structural investigation of the above compounds by X-ray diffraction method. 3) Phase transition and thermal stability studies by the TG, DTA and high temperature X-ray methods. 4) Investigation of some of the alkaline earth-europium(II)-apatite solid solution systems.

Results and Implications to Date

During the last few years growing interest in the investigation of apatites can be seen in the literature. The main reasons for this interest are the biological aspects of these materials, apatite being the main component of mineral bones, and also some industrial applications where apatites serve as hosts for ions having fluorescence properties. The volume of investigations dealing with apatites is greatly expanding because of the great variety of possible composition of the metal (M), non-metal (X) and halide (Y) constituents of the $\text{M}_5(\text{XO}_4)_3\text{Y}$ compounds.

At the basis of these studies are the crystal structure determination of the hydroxy-, fluoro-, and chloro-apatites of calcium. All the other apatites with different metal and non-metal ions can be related to these three prototypes. The information obtained from their crystal data enables one to identify other apatites, to classify them and predict their formation and characteristic properties.

In the case of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ it was found⁴ that this compound crystallizes in a hexagonal unit cell containing two formula units in each cell. The structure is built up by triangles of Ca^{++} ions and in the center of these triangles are located the F^- ions, forming columns parallel to the c axis. The six tetrahedral PO_4 groups of each cell are structurally equivalent. In the case of the chloroapatite,^{5,6} because of the larger size of Cl^- , these ions are located halfway between the mirror planes of the crystal. Chloroapatite has therefore a monoclinic unit cell, which can be derived from a hexagonal cell by doubling one of the hexagonal a axes. Above 200°C the monoclinic $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ changes to the hexagonal apatite structure. The hydroxyapatites also have the hexagonal structure⁷ but the OH groups are located above the calcium triangles in a twofold statistical disorder.

In order to improve the structural study of the apatites, and for the purpose of magnetic and fluorescence investigations, efforts have been made to prepare the apatites in single crystal form. The most widely used methods are the growing of the crystals from melt or by the hydrothermal bomb methods.³

A great number of apatites have been synthesized by varying the metal and non-metal constituents. There are known apatites of the form $M_5(XO_4)_3Y$ in which the metal ions are of the alkali, the alkaline earth or rare earth metals and also Pb and Cd,^{8,9,10} and where $X = P, As, V, Cr, Mn, Si$ and Ge and finally Y can be one of the halide ions or OH^- .¹¹⁻¹⁵ Solid solutions formed between the different apatites have also been reported in the literature.^{16,17}

It is known that divalent europium behaves in its compounds similarly to the alkaline earth metals. It was decided therefore to prepare the apatites of Eu^{++} in order to study their structural and other chemical and physical properties and the relationship of these properties to other known apatites.

Preliminary Results

The following results were obtained before the start of this project and describe our first studies in the field of the Eu^{++} -apatites.

The preparation and crystal data of $Eu_5(PO_4)_3OH$

Preparation:

The preparation of the above compound was carried out by treating $EuSO_4$ with a solution of Na_3PO_4 . $EuSO_4$ was prepared by dissolving Eu_2O_3 in hydrochloric acid and the solution through a Jones reductor into $8 NH_2SO_4$.¹⁸

To a certain amount of $EuSO_4$ a Na_3PO_4 solution (0.004 M) in excess was slowly added. The suspension was then heated on an electric plate and continuously stirred for 8 hours, at the end of which the colour of the mixture changed from white to yellow. The suspension was then filtered and the solid part dried in a desiccator.

The composition of $Eu_5(PO_4)_3OH$ obtained by this method was checked by determining the phosphorous content of the compounds by colorimetric methods. The results of these determinations showed 8.94% P in the samples, the theoretical value being 8.75% P. The possible sodium content of the samples was checked by atomic absorption method, showing 1.5% Na-content.

X-ray data:

Powder diffraction data obtained by a Philips Diffractometer using $CuK\alpha$ radiation have shown that the X-ray pattern of the $Eu_5(PO_4)_3OH$ can be indexed on the basis of a hexagonal cell with lattice constants $a = 9.73 \pm 0.02 \text{ \AA}$ and $c = 7.22 \pm 0.01 \text{ \AA}$. In table 1 are listed the powder diffraction data. Examination of these data shows that $Eu_5(PO_4)_3OH$ is isomorphous with the alkaline earth apatites.

Table 1

Powder diffraction data of $\text{Eu}_5(\text{PO}_4)_3\text{OH}$

| h k l | d Å | $\sin^2\theta_{\text{obs.}} \times 10^4$ | $\sin^2\theta_{\text{calc.}} \times 10^4$ | I _o |
|-------|-------|--|---|----------------|
| 2 0 0 | 4.20 | 337 | 335 | 25 |
| 1 1 1 | 4.04 | 364 | 365 | 20 |
| 0 0 2 | 3.60 | 458 | 456 | 15 |
| 1 0 2 | 3.31 | 541 | 540 | 30 |
| 2 1 0 | 3.18 | 586 | 586 | 35 |
| 2 1 1 | 2.90 | 703 | 700 | 100 |
| 1 1 2 | | | 707 | |
| 3 0 0 | 2.81 | 753 | 754 | 45 |
| 1 1 3 | 2.16 | 1273 | 1277 | 30 |
| 2 2 2 | 2.01 | 1461 | 1461 | 25 |
| 3 1 2 | 1.96 | 1542 | 1542 | 15 |
| 2 1 3 | 1.92 | 1609 | 1612 | 10 |
| 3 2 1 | 1.966 | 1703 | 1705 | 15 |
| 4 1 0 | 1.836 | 1759 | 1759 | 8 |
| 3 0 3 | 1.817 | 1796 | 1780 | 10 |
| 4 0 2 | | | 1796 | |

Results obtained in the present project

As a continuation of the studies done in the preliminary research it has been decided to start this project with the preparation and investigation of $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$.

The preparation and crystal data of $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$

Preparation:

All the attempts to prepare the above compound by a direct reaction of EuCl_2 and Na_2HAsO_4 or by treating EuSO_4 with $(\text{NH}_4)_2\text{HAsO}_4$ failed.

$\text{Eu}_5(\text{AsO}_4)_3\text{OH}$ could be successfully prepared, when EuSO_4 (prepared as in the case of $\text{Eu}_5(\text{PO}_4)_3\text{OH}$) was treated with a solution of Na_2HAsO_4 in the presence of an excess of NaOH . The stoichiometric amounts of EuSO_4 and Na_2HAsO_4 together with NaOH were boiled on an electric plate 1 - 2 hours. During this treatment argon gas was passed through the solution. When boiling was ended the solid part of the mixture was filtered and dried.

Chemical analysis of the arsenic content of the samples agreed very well with the composition and despite the excess of Na^+ ions in the mixture, atomic absorption analysis of the samples showed less than 1% Na^+ .

X-ray data:

Powder diffraction data of the samples have shown that $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$ has the apatite-like hexagonal structure. Powder data of the compound is listed in table 2. The lattice constants calculated are: $a = 9.95 \pm 0.02 \text{ \AA}$ and $c = 7.35 \pm 0.01 \text{ \AA}$. These constants give higher values than those obtained for $\text{Eu}_5(\text{PO}_4)_3\text{OH}$ because of the insertion of the bigger AsO_4^{3-} ions.

Table 2

Powder diffraction data of $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$

| h k l | d \AA | $\sin^2 \theta_{\text{obs.}} \times 10^4$ | $\sin^2 \theta_{\text{calc.}} \times 10^4$ | I_o |
|-------|----------------|---|--|-------|
| 1 1 0 | 4.96 | 241 | 240 | 10 |
| 2 0 0 | 4.30 | 320 | 320 | 12 |
| 0 0 2 | 3.66 | 441 | 440 | 18 |
| 1 0 2 | 3.37 | 520 | 520 | 20 |
| 2 1 0 | 3.25 | 561 | 560 | 25 |
| 2 1 1 | 2.96 | 679 | 670 | 100 |
| 1 1 2 | 2.96 | | 680 | |
| 3 0 0 | 2.87 | 719 | 720 | 35 |
| 4 0 1 | 2.06 | 1396 | 1390 | 25 |
| 2 2 2 | | | 1400 | |
| 3 1 2 | 2.00 | 1477 | 1480 | 10 |
| 2 1 3 | 1.95 | 1548 | 1550 | 20 |
| 3 2 1 | 1.910 | 1625 | 1630 | 12 |
| 4 1 0 | 1.879 | 1680 | 1680 | 10 |
| 3 0 3 | 1.857 | 1720 | 1710 | 10 |
| 4 0 2 | | | 1720 | |
| 0 0 4 | 1.839 | 1753 | 1760 | 8 |

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List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

Project Title: ANALYTICAL DETERMINATION OF MINUTE QUANTITIES OF RARE EARTHS

Principal Investigator: Dr. Renata Reisfeld

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. O. Menis

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

This project will involve the high precision measurements, by spectrofluorimetry, of small quantities of rare earths in certain materials within the NBS Standard Reference Program. Precise methods are needed for the determination of the individual rare earths, i.e., europium, samarium, dysprosium, gadolinium, lanthanum, etc., in various media and in the presence of other rare earths. The application of fluorescence to these analyses has not been too extensive, principally because of certain limitations of commercially available instruments. A new and modified spectrofluorimeter, developed and assembled by this laboratory which will increase the sensitivity of detection of the individual lanthanides, will be utilized in the development of the analytical methods that are based on excitation spectra. Rare earths are becoming increasingly more important constituents of such NBS Standard Reference Materials as glasses, ceramics, clays and, to some extent, ferrous-base alloys. The proposed research is quite applicable to the production of industrially important reference standards.

Results and Implications to Date

This project is monitored by Dr. O. Menis of the Analytical Coordination Chemistry Section and has an important relationship with the work of that Section.

The Analytical Coordination Chemistry Section at NBS has recently proposed and begun research in a program designed to produce a series of fluorescence standards. These standards would be extremely useful in very diverse fields of interest: in practical and applied areas such as clinical chemistry, environmental science, forensic medicine and science, analytical and organic chemistry and even the post office; and in theoretical research done by physicists and physical chemists. The use of these standards would enable various laboratories to collect, store, evaluate and compare analytical techniques, data, procedures and results under known experimental and comparable conditions so necessary for the dissemination of meaningful information.

A. Rare Earths

a. Analytical Applications

The initial phase of the research was concerned with the fluorescent analytical determinations of various rare earth ions in different glass matrices to establish emission and excitation spectra, fluorescence intensity dependence on ion concentration, matrix

effects and fluorescence decay times (1-8).

The rare earth concentrations may be determined analytically since the fluorescence intensity is proportional to the rare earth concentration. The best emission and excitation wavelengths for the determination are given in Table I. Thallium and lead are included here, but will be discussed later with Ce(III). The rare earths, in general, have several emission peaks which may also be used for the analyses if convenient or necessary due to interferences by other species. Maximum intensities, however, are obtained with the suggested peaks summarized in Table I.

We are also compiling corrected spectra, transition assignments and relative intensities (see for example Eu(III) data in Table II) which will be published in the near future.

b. Matrix Effects

The coulombic potential of the active ion is approximated by

$$(1) \quad F = -\frac{Z_i}{r^2} \quad \text{where } F = \text{coulombic potential}$$

$r = \text{ionic radius}$

$Z_i = \text{charge on the ion}$

Calculations of the coulombic potentials for various ions are presented in Table III and show that the rare earth ions enter the glass matrix only as network modifying ions.

The usual narrow band emission spectra of the rare earths are usually due to intra-configurational f shell electronic transitions which are LaPorte forbidden for centrosymmetric fields. In a solid or liquid where the center of symmetry is destroyed or lowered, the transitions become allowed and, due to mixing of f orbital transitions and interactions with the effective crystal field of the glass hosts, broadening and splitting of the RE energy levels occur.

According to ligand field theory, an increase in the separation of the crystal field split degenerate levels indicates an increase in the ligand field seen by the rare earth ions. In cases of transitions between two non-degenerate energy levels, an increase in the outer ligand field causes the two levels' displacement towards lower energy levels. Stronger outer perturbations will induce energy level shifts towards longer wave lengths as shown in Table IV for the shifts of the major emission peaks of Eu(III) and Sm(III). The stronger perturbations caused by the borate or phosphate relative to silicate (also approximated from the Born equation (2)) shift the most intense emission bands to longer wavelengths as expected.

$$(2) \quad E = \sum \frac{Z_i Z_j}{r_{ij}^n} + \frac{b}{r^n}$$

where $E = \text{coulombic potential}$
 $Z_i = \text{charge on RE ion}$
 $Z_j = \text{charge on matrix ion}$
 $r_{ij} = \text{distance between opposite charges}$
 $b = \text{constant}$
 $n = 4 \text{ to } 10$

In addition, weaker interactions between the rare earths and the silicate matrix result in less fluorescent center interactions, fewer radiationless transitions, and thus less concentration quenching. For example, 0.5 wt.% samarium in borate showed concentration quenching while 3 wt.% of samarium in silicate showed no concentration quenching (9).

Table V also indicates the higher intensities of the emission peaks of the RE ions in borate glasses compared to those in silicate glasses, in agreement with their higher 'effective' coulombic crystal field (2).

Further evidence for rare earth - matrix interactions were obtained by the measurement of fluorescent decay times, presented in Table VI. On the average, fluorescent decay times are shorter in the order: borate < phosphate < silicate, showing better facilitation of energy dissipation through stronger interactions between the rare earths and matrices in the order borate > phosphate > silicate.

The dependence of quenching, intensities, fluorescence decay times, and shifts of major emission peaks may also be explained if one looks at the infra-red stretching frequencies and bond lengths for the active ion - oxygen in the matrices, Table VII. The higher the stretching frequencies and more comparable they are to the energy gaps of the RE transitions, the larger is the probability of phonon assisted energy transfer from the RE to the matrix with the result of increased radiationless transitions.

The majority of this work has been done on rare earths in the plus three oxidation state. Reduction of the rare earths yields ions in the plus two oxidation state and give broad spectra. Further work is planned on this aspect of rare earth chemistry.

B. Non-Rare Earth Metals.

We have also begun exploratory research on other metal ions in glasses, such as cerium (although Ce(III) is a rare earth, it is discussed here because of spectral similarity to other metals), lead, copper, and manganese. We have obtained results for the fluorescence intensities of lead and cerium (III) as a function of concentration and again straight line dependence was observed. The broad spectra observed for these metal ions increase applicability of these glasses as standards since bandwidths of the exciting peaks determine instrumental bandwidth minima. Many clinical laboratories do not have 'research type' spectrofluorimeters. In such cases, the broad bandwidths of the instruments necessitates the use of standards with broad excitation and emission spectral bands. These broadened spectra are due to $d^* \rightarrow f$ and $p^* \rightarrow s$ transitions rather than the narrower $f^* \rightarrow f$ transitions which one observes for the rare earths in the plus three oxidation state. Interactions of the metal ions with the glass matrices would further broaden the already broad spectra.

Cerium equilibrates to form a Ce(III) - Ce(IV) couple independent of the oxidation state of the starting cerium compound. Stroud reports (11) that Ce(III) photo-oxidizes to Ce(IV), however intensities with xenon lamps are not as high as mercury lamps and investigations are presently under way to determine the stability of the Ce(III) glasses. In addition, quantitative reduction of Ce(IV) to Ce(III) has been accomplished using mannitol (12). A plot of absorbance vs. concentration for Ce(III) produces a straight line indicating quantitative reduction whereas the presence of Ce(IV) would produce deviations from linearity.

C. Energy Transfer.

Energy transfers have been observed between donor (emission) and acceptor (excitation) sites between two different rare earth ions. Objectives of this research include the enhancement of emission intensities and excitation of species at higher wavelengths and thus

lower energies so that problems of photo-oxidation and other side reactions are not present.

Summaries of this work are found in references 2, 13 and 14. The relative fluorescence intensities have been obtained with Eu(III) alone and Eu(III) plus Sm(III) in phosphate when excited at 420 nm (Sm(III) excitation). The emission intensity of the Eu(III) is definitely increased by emission-excitation overlap. Other pairs investigated include Gd(III) - Sm(III), Gd(III) - Tb(III) and Er(III) → Tm(III). It was found that energy transfer occurs by dipole - dipole or dipole - quadrupole interactions.

D. Quantum Efficiencies

The determination and presentation of quantum efficiencies with any standard is a pre-requisite for its widespread acceptance. Quantum efficiencies may be determined in several ways:

1. photometrically in absolute units by measuring photons or energy absorbed and photons or energy emitted
2. photometrically using a comparative method with an accepted standard such as quinine sulfate
3. fluorescence decay time measurements, and
4. calorimetric techniques

Quantum efficiencies are most rapidly determined experimentally by methods 2 and 3 and these were used in our studies. We have started by determining the quantum efficiency of Eu(III) in silicate (15) and phosphate (16) matrices. The quantum efficiency depends on the wavelength of excitation since major fluorescence generally occurs from the first excited state, the 5D_0 in the case of Eu(III). Excitation to higher energy levels results in a greater probability of radiationless transitions to the first excited state, thus decreasing the quantum efficiency. Very weak fluorescence may also be observed from higher excited states (17).

Use of a 'corrected spectrofluorimeter' on loan from NBS greatly facilitated the measurement of comparative quantum efficiencies. The instrument was developed by G.K. Turner Associates (18) and formula used for quantum efficiencies, later modified by Fletcher (19) is:

$$(3) \quad Q_u = Q_s \frac{A_u OD_s \lambda_s n_u^2}{A_s OD_u \lambda_u n_s^2}$$

where Q = quantum efficiencies
A = area under emission peaks
OD = absorbance at excitation
λ = excitation wavelength
n = refractive indices
u,s refers to unknown and standard respectively

Preliminary data indicate a quantum efficiency of 1.05 for the $^5D_0 \rightarrow ^7F$ transitions when excited at 578.5 nm (a value of approximately 1.00 was expected).

Fluorescence decay time measurements also give quantum efficiencies according to equation (4):

$$(4) \quad Q = \frac{\tau_{\text{exp}}}{\tau_{\text{nat}}}$$

where Q = quantum efficiency
 τ_{exp} = measured decay time
 τ_{nat} = theoretical decay time

The theoretical decay time, τ_{nat} , may be calculated from the absorption spectrum according to equation (5):

$$(5) \quad 1/\tau_{\text{nat}} = 2.88 \times 10^{-9} n^2 (g_1/g_u) \nu_0^2 \int_{\nu_I}^{\nu_F} \epsilon(\nu) d\nu$$

where n = refractive index
 g_1 = and g_2 are the degeneracies of the lower and upper states respectively
 ν_0 = absorption maximum in wavenumbers
 ϵ = molar absorption coefficient as a function of wavenumber
 ν_I and ν_F are wavenumbers which define the beginning and the end of the absorption band.

τ_{exp} for Eu(III) in silicate and phosphate glasses have been measured and found to be 2.66 ± 0.035 and 2.78 ± 0.077 milliseconds respectively (15,16). Computer programming is currently being done to obtain best gaussian fits for the absorbance spectra, so that τ_{nat} , transition probabilities and energy level populations can be determined.

Further information about transition probabilities may be determined by calculating the oscillator strength, f , which is related to the theoretical decay time by equation (6):

$$(6) \quad \tau_{\text{nat}} = \frac{1.5 \times 10^{-8}}{f \nu^2}$$

It is proportional to the dipole strength of the transition, which is in turn a measure of the difference between the degree of dipolar oscillation of the electron in the two states involved in the transition.

One recent research program has been concerned with use of thallium chloride in pressed KCl discs as quantum efficiency ($QE = .52$ (20)) standards (21). It obeys the Beer-Lambert law and use of discs is inherently easier experimentally than production of cuvette type blocks. The emission and excitation spectra show somewhat wider bandwidths than do the rare earths.

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List of Publications that Resulted from the Project

1. "Luminescent Characteristics of Silicote Glasses Doped with Rare Earths under Monochromatic Excitation", R. Reisfeld, A. Honigbaum, G. Michaeli, L. Harel and M. Ish-Shalom, Israel J. Chem., 7, 613 (1969).
2. R. Reisfeld, E. Greenberg, L. Kirshenbaum and G. Michaeli, Proc. 8th Rare Earth Res. Conf., Vol. II, p. 743 (1970).
3. "The Determination of Europium(III) in Borate Glasses", R. Reisfeld and E. Greenberg, Anal. Chim. Acta, 47, 155 (1969).
4. "Determination of Gadolinium in Sodium Borate Glasses", R. Reisfeld and E. Biron, Talanta, 17, 105 (1970).
5. "Determination of Dysprosium in Borate Glasses", R. Reisfeld, E. Greenberg and S. Kraus, Anal. Chim. Acta, 51, 133 (1970).
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7. "The Determination of Thulium(III) in Borate and Phosphate Glasses", R. Reisfeld and Y. Eckstein, Anal. Chim. Acta, 56, 461 (1971).
8. "Fluorescent Characteristics of Samarium(III) and Europium(III) in Metaphosphate Glasses", R. Reisfeld and L. B. Kirshenbaum, Israel J. Chem., 8, 103 (1970).
9. "Thalium Doped Potassium Chloride Discs as UV Fluorescence Standards", R. Reisfeld, A. Hongibaum and R. A. Velapoldi.
10. "Spectral Characteristics and Quantum Efficiencies of Europium(III) in Phosphate Glasses", R. A. Velapoldi, R. Reisfeld and Lea Boehm, Proe. 9th Rare Earth Research Conference, Volume II, 488 (1971).
11. "Trans. Probabilities of Europium (III) in Phosphate Glasses", R. Reisfeld, R. A. Velapoldi, Lea Boehm and M. Ish-Shalom, J. Phys. Chem., 75, 3980 (1971).
12. "Quantum Efficiencies and Radiationless Transitions of Europium(III) in Phosphate Glasses", R. Reisfeld, R. A. Velapoldi and Lea Boehm; submitted to J. Phys. Chem.

13. "Luminescent Quantum Efficiencies of Gadolinium and Terbium in Borate Glasses and the Mechanism of Energy Transfer Between Them", R. Reisfeld, E. Greenberg, R. A. Velapoldi and B. Barnett; accepted for publication J. Phys. Chem.
14. "Quantum Efficiencies and Transition Probabilities of Europium(III) in Silicote Glasses", R. A. Velapoldi, R. Reisfeld and Lea Boehm; submitted to J. Solid State.

Table I

Excitation and Emission Wavelengths for Metal Ions in Glasses
Producing Most Intense Responses

| Metal Ions | Excitation (nm) | Emission (nm) | Glass Matrix |
|------------|--------------------|------------------|-------------------|
| <hr/> | | | |
| Er(III) | 365 | 546 | Borate |
| Dy(III) | 365 | 578 | " |
| Tb(III) | 378 | 543 | " |
| Eu(III) | 394 | 617 | " |
| Eu(III) | 394 | 612 | Phosphate |
| Eu(III) | 394 | 610 | Silicate |
| Tm(III) | 265 | 454 | Borate |
| Gd(III) | 274 | 312 | Borate |
| Pb(II) | 285 | 365 | Borate |
| Ce(III) | 310 | 369 | Borate |
| Tl(I) | 248 | 308 | KCl, pressed disc |

Table II

Transition Assignments and Relative Intensities of Major Emission and Excitation Bands for Eu(III) in a Silicate Matrix

Emission

| $\nu \times 10^{-3}$ | assignment* | relative intensity |
|----------------------|-------------------------|--------------------|
| 17.25 | $5D_0 \rightarrow 7F_0$ | .0374 |
| 16.88 | $5D_0 \rightarrow 7F_1$ | .2058 |
| 16.38 | $5D_0 \rightarrow 7F_2$ | 1.0000 |
| 15.25 | $5D_0 \rightarrow 7F_3$ | .0606 |
| 14.42 | $5D_0 \rightarrow 7F_4$ | .0308 |
| 14.16 | $5D_0 \rightarrow 7F_4$ | .1002 |
| 13.24 | $5D_0 \rightarrow 7F_5$ | .0090 |
| 12.71 | $5D_0 \rightarrow 7F_6$ | .0381 |

Excitation

| | | |
|-------|-------------------------|-------|
| 32.84 | $7F_1 \rightarrow 5F_3$ | .480 |
| 31.13 | $7F_0 \rightarrow 5H_0$ | .251 |
| 27.58 | $7F_0 \rightarrow 5D_4$ | .733 |
| 26.18 | $7F_1 \rightarrow 5G_3$ | .753 |
| 25.38 | $7F_0 \rightarrow 5L_6$ | 1.000 |
| 24.06 | $7F_0 \rightarrow 5D_3$ | .375 |
| 21.54 | $7F_0 \rightarrow 5D_2$ | .353 |
| 18.99 | $7F_0 \rightarrow 5D_1$ | .252 |
| 18.75 | $7F_0 \rightarrow 5D_1$ | .264 |
| 17.29 | $7F_0 \rightarrow 5D_0$ | .162 |
| 16.96 | $7F_1 \rightarrow 5D_0$ | .214 |

* W. T. Carnall, P. R. Fields and K. Rajnak, J. Chem. Phys., 49, 4450 (1968);
G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals",
Interscience Publishers, New York, N. Y., 1968, pages 242-7.

Table III
Ionic Field Strengths of Cations in Glasses (2)

| Ion | Ionic Radius, Å (9,10) | Field Strength z/r^2 | Effect |
|---------|---------------------------|---------------------------|------------------------|
| B(III) | 0.20 | 75.0 | Network Forming Ions |
| P(V) | 0.34 | 43.2 | |
| Si(IV) | 0.41 | 23.8 | |
| Ca(II) | 0.99 | 2.04 | Network Modifying Ions |
| Na(I) | 0.95 | 1.11 | |
| Eu(III) | 0.95 | 3.32 | |
| Sm(III) | 0.964 | 3.23 | |
| Tb(III) | 0.923 | 3.52 | |
| Dy(III) | 0.908 | 3.64 | |
| Gd(III) | 0.938 | 3.41 | |

Table IV

Shifts of Major Europium and Samarium Emission
Peaks as a Function of Matrix

| Matrix | Emission Maximum, nm | |
|-----------|----------------------|---------|
| | Eu(III) | Sm(III) |
| Silicate | 610 | 596 |
| Phosphate | 612 | 601 |
| Borate | 617 | 605 |

Table V

Effects of Glass Matrix on Fluorescence Intensities
of the Rare Earth Ions (1 wt.%)

| Ion | Fluorescence Ratio, Silicate/Borate | |
|---------|-------------------------------------|-----|
| | | |
| Eu(III) | | .30 |
| Sm(III) | | .65 |
| Tb(III) | | .76 |
| Dy(III) | | .74 |
| Gd(III) | | .59 |

Table VI
Average Fluorescence Decay Times of Rare Earths in Various Matrices
(RE Concentration is 1 wt.%)

| Ion | Silicate decay time (ms) | Phosphate decay time (ms) | Borate decay time (ms) |
|---------|--------------------------|---------------------------|------------------------|
| Eu(III) | 2.55 | 2.32 | 2.05 |
| Sm(III) | 2.60 | 1.87 | 1.60 |
| Tb(III) | 3.90 | 3.30 | 2.80 |
| Dy(III) | 0.95 | 0.87 | 1.00 |
| Gd(III) | 4.32 | 5.25 | 4.30 |

Table VII
Infrared Stretching Frequencies and Bond Lengths for the Active
Ion - Oxygen Interaction in the Matrix (2)

| Matrix | Stretching Frequency (cm^{-1}) | Bond Length (\AA) |
|---------------------|---|------------------------------|
| Silicate (Si-O) | 1010-1115 | 1.62 |
| Metaphosphate (P-O) | 1140-1300 | 1.57 |
| Borate (B-O) | 1310-1380 | 1.39 |

A.6. Standard Reference Materials Program

Project Title: MOSSBAUER SPECTROSCOPY STANDARDS FOR CARBON STEELS

Principal Investigator: Dr. Moshe Ron

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: B. Christ

NBS Institute or Center and Division: Institute for Materials Research
Metallurgy Division

Summary Description of Project Goals

This project will involve the preparation and characterization of a graded series of iron-carbon alloys containing up to 1 per cent carbon, for use as NBS Standard Reference Materials in Mossbauer Spectroscopy. The specimens will be heat-treated at different temperatures by quenching and then tempering from room temperatures up to approximately 700°C with different cooling rates. It is possible then by this Mossbauer technique to define and distinguish between the various phases which exist together in steels, as a result of this heat treatment. This valuable metallographic tool is therefore useful for the advancement of fundamental understanding of atomic structure and phase distributions which occur in a wide range of ferrous-base alloys.

Results and Implications to Date

a. Specifications of Requirements for Standards

The natural abundance of isotope Fe⁵⁷ in iron (about 2 atomic per cent) is generally sufficient in an iron base alloy to enable the utilization of the Mossbauer technique in experimental measurements.

Compilation of data based upon standard samples utilizing the Mossbauer effect calls for careful considerations which are new and specific for this method.

An iron atom transformed from the martensite into the carbide phase can be directly detected. Also an iron atom transformed from one carbide phase to another or any change in the atomic environment is definitely detectable in the spectrum. In many cases, however, the resolution is poor and special measures must be then taken in order to increase the sensitivity sufficiently to make the method applicable. A typical situation is one in which the carbide grown by tempering is not sufficiently pronounced in the spectrum of tempered martensite but can easily be detected if first extracted chemically.

Since the method is entirely new and almost no supporting data exist, one must achieve high reproducibility of results and check them carefully against all the parameters that are reasonable over as wide a range as possible. A basic understanding of the controlling mechanism enables the performance of an expedient analysis in terms of each parameter.

The Fe-C alloy, which is an interstitial alloy, is characterized by the fact that its state and properties are dependent on the whole sequence of previous heat treatments. Essentially the process is the identification of the various phases which exist simultaneously at different states - resulting from different heat treatments. The use of the extraction procedure makes it possible to analyze the carbides with a high sensitivity due to the elimination of the screening effect of the matrix. This study was carried out on a pure Fe-C alloy of 0.7% wt carbon and on commercial steels containing alloying impurities such as Mn and Si. Manganese is known to be a carbide forming element, while silicon tends to retard the carbide formation. The physical background and criteria concerning carbide formation are described in one of the following sections.

When the physical background and the different transformation mechanisms occurring in the carbides (nucleation and growth) as reflected in the spectrum are sufficiently understood, it is possible to establish a system of calibration standards.

b. The Physical Background

Mossbauer spectroscopy: The basic principles of the Mossbauer effect spectroscopy are here briefly reviewed. A γ -ray emitted or absorbed due to a transition between the excited and ground nuclear states of an atom bound in a crystalline solid can occur in a recoil-free fashion. This occurs because the crystal as a whole takes up the recoil momentum so that the γ -ray possesses all the energy of the nuclear transition. Three terms of the spin Hamiltonian are relevant for describing the nuclear energy level. These are the electric monopole, magnetic dipole and electric quadrupole hyperfine interactions expressed as isomer shift Zeeman and quadrupole splittings. Other characteristic features of the Mossbauer patterns concerning various phases, or mostly mixtures of phases, are given here.

When the fcc γ -phase is transformed into bcc α -phase the carbon solubility drops by a factor of 100. As a result of the diffusionless martensitic transformation a supersaturated solid solution is formed with carbon arrested interstitially. This is the most striking feature of the Fe-C interstitial alloy.

The compositions considered are restricted to hypo-eutectoid or nearly eutectoid composition, 0.75 - 0.7 wt.% carbon.

A highly supersaturated solid solution results from quenching. The carbon segregation processes begin immediately. These processes may be nucleation, clustering, precipitation, or even a sluggish component of a phase change. In the martensitic stage the following components are known to appear in the Mossbauer spectrum ⁽¹⁾: M_I - a six line component representing the iron atoms which stay almost unaffected by the presence of the interstitial carbon. This component has the same positions and pattern as has metallic α -iron. M_{II} and M_{III} are components belonging to the iron atom in the close vicinity of an interstitial carbon atom ⁽¹⁾. The first is contributed by the four iron atoms in the (001) plane. The second arises from the two iron atoms that are pushed away by the carbon in the [001] direction, which is the c direction of the distorted B.C.T.-like cell. The effect of the carbon concentration on those components was shown in a previous publication ⁽¹⁾.

A doublet centered at 0.34 ± 0.3 mm./sec. relative to metallic Fe⁵⁷ has already been described (2). It appears in the central part of the spectrum. It appears generally at the expense of the M_{III} component but may exist together with it. The detection of the doublet inside the parent martensite is still difficult because of the screening effect of the matrix. In order to overcome this difficulty, chemical extraction of the carbides is used.

Recently it was suggested (3) that the vacancy concentration quenched in from the austenization treatment controls the amount of carbon segregated by nucleation.

The number of nucleants created prescribes, of course, the rate and the completeness of the carbide precipitated during tempering.

In the investigation new, previously unknown, results were found:

1. Differentiating between activation energies for nucleation and for growth.
2. The evaluation of the difference between these energy values.
3. A vacancy-carbon interstitial interaction mechanism that controls the precipitation kinetics.

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List of Publications that Resulted from the Project

1. M. Ron, Z. Mathalone, S. Niedzwiedz, The Vacancy-Interstitial Impurity Interaction Influence on Precipitation, Acta Crystal A25, (1969) S51, Submitted to the Eighth International Congress of Metallurgy.
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5. M. Ron, Z. Mathalone, S. Niedzwiedz, The Influence of Austenization on the Kinetics of Tempering - Mossbauer Study (in publication).
6. M. Ron, Z. Mathalone, The Hyperfine Structure of Fe₃C (to be published).

A.6. Standard Reference Materials Program

Project Title: CALIBRATION MATERIALS FOR THE MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Principal Investigator: Dr. Michael Schieber

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. G. Candela

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

A research program was proposed, which would lead to the continuous production of sets of three crystal spheres, each of them containing various amounts of Gd^{3+} , which were to serve as calibration materials for magnetic susceptibility measurements. The crystals proposed were Gd_2O_3 , $Na_{0.5}Gd_{0.5}MoO_4$ and $Na_{0.50}Gd_{0.01}Y_{0.49}MoO_4$. The crystals were to be calibrated in Jerusalem each against the others and all against freshly prepared $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ which is a good standard material⁽¹⁾ but is unstable with time. Finally, a program of mass production of the calibration materials would be offered to the National Bureau of Standards for the purpose of secondary standards for susceptibility measurements to be sold as Standard Reference Materials.

The growth of the crystals were to be attempted from multi-component molten salts solution (flux method). The crystals would be identified by x-ray powder diffraction and accurate determination of the lattice parameter. The content of Gd^{3+} would be determined by classical chemical analysis and in the case of $Na_{0.5}Gd_{0.5}MoO_4$ was to be determined by electron-proton resonance measurements. All the crystals were to be worked into spheres and then etched in order to remove any possible ferromagnetic contamination. The reproducibility of the production of spherical crystals for every successful process of growth would be checked for ten consecutive runs and the magnetic susceptibility of spheres at at least three fixed temperature points would be reported.

Alternatively an attempt to produce palladium cylinders of high purity might also be made by subjecting commercial high purity palladium to a treatment of solid state electrolysis and annealing it afterwards in a very high vacuum, or refining it by electron beam zone melting. The efficiency of purification would be checked by measuring the electrical resistivity ratio between 4.2 and 295°K and correlating it with the magnetic susceptibility of the Pd. The mechanism of purification would be studied by making kinetics studies of the purification method using the resistivity ratio and susceptibility as the determining characterization parameter.

Results and Implications to Date

The aims of the program have been to develop the production in situ of crystals for (a) the calibration of the magnetic moments with varying magnitudes of the saturation magnetization and for (b) the calibration of the magnetic fields.

(a) After several preliminary trials garnet type crystals have been selected. Single

crystals of $\text{Y}_{3-x}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$ called B-Y and of $\text{Yb}_{3-x}\text{Ca}_x\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$ called B-Yb have been grown with x varying between 0.6 and 1.5, B-Y crystals having a low magnetic anisotropy were mostly suited for calibration purposes. The saturation magnetization achieved at relatively low fields of 1000-1500 Oe, varies at room temperature between 17 for x=0.6 to 4 emu/g for x=1.5. The value 4.0 emu/g should be compared with that of 54.0 emu/g for metallic nickel, used for calibration purposes. The B-Y crystals grown by flux method are large enough for calibration purposes, since they can be used as-grown. They weigh 20 to 200 mg. The accuracy of measurements is 3×10^{-3} emu. An accurate determination of x has been achieved by measuring the lattice parameter, Curie temperature, and magnetization at liquid helium and room temperatures. The same set of measurements have been performed also on ceramic polycrystalline samples where the value of x is known. Some preliminary characterization measurements have been performed using x-ray fluorescence and atomic absorption measurements. The accuracy of the determination of x by the non-magnetic measurements is much lower, i.e. a variation of about 10% against 1% using many measurements and improved statistics. The accurate knowledge of x is important only from a scientific point of view, since it allows a better understanding of the magnetic interactions in diamagnetically diluted ferrimagnetic systems predicted by the Nowik theory. For calibration purposes it is important to measure each sample separately for absolute calibration purposes and it is therefore not important to know x better than it has been determined so far.

One set of B-Y has been prepared and calibrated by measuring its moment between 90 and 300°K. This set will be sent to Dr. G. Candela, the NBS monitor of this project.

(b) After considering the paramagnetic crystals of $\text{Na}_{0.5}\text{Gd}_{0.5}\text{MoO}_4$, crystals $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ have been grown, using the flux method. The magnetic field is calibrated by measuring the magnetic moment of a material with a known magnetic susceptibility. In this case it is necessary to grind the crystals into spheres, in order to account for the factor of the demagnetization. The spheres produced so far are smaller than the minimum weight of 20 mg we wanted to achieve. The accuracy by which we measure the magnetic susceptibility is 3×10^{-7} emu for a magnetic field of 15 KOe.

The accuracy for both magnetic moments and magnetic susceptibility can be improved by repeating the measurements many times on the same sample and calculating the statistical average. It is also desired to measure all samples at liquid helium and higher temperatures.

List of Publications that Resulted from the Project

1. "The Magnetic Interactions in Diluted Garnets", A. Grill and M. Schieber; Presented at the International Conference on Magnetism Grenoble 1970. To be published in the J. de Physique, supplement to no. 2-3, 32 (1971) C1-195.
2. "The Crystal Growth and Magnetic Characterization of Diluted Garnets", M. Schieber, A. Grill and Y. Avigal; Presented at the International Conference of Crystal Growth, Marseille, 1971, to be published in the J. of Crystal Growth.

Project Title: CHEMICAL MICROSTANDARDS

Principal Investigator: Dr. Gabriella Schmuckler

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. D. H. Freeman

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

This project involves the development and characterization of new microstandard reference materials by means of homogeneous substitution reactions with homogeneous copolymers of styrene and divinylbenzene. Pertinent aspects of homogeneous sulfonation and chloromethylation will be investigated. As the mechanisms of these reactions are understood and controlled, ion-exchangers having functional groups, such as amines, amino-acids or carboxylic acids, will be prepared. This work will be coordinated with identified needs of the Standard Reference Materials Program.

Results and Implications to Date

Ion exchange microstandards must be prepared with special care. Commercially available ion-exchangers are unsuitable as standards because of their marked heterogeneity and the variations in composition from bead to bead. If more uniform and better defined spherical ion-exchange beads are to be obtained, the diameter of which can be correlated to the concentration of cations or anions adsorbed, all the chemical modifications which are performed in the course of the preparation of each ion-exchanger concerned should be subjected to close scrutiny in order to gain a better understanding of the reactions involved, with a view to bringing the beads as near to uniformity as possible. Such reactions generally relate to the electrophilic substitutions on each aromatic ring in the copolymer and their control.

Accordingly, the swelling properties of single copolymer beads were investigated in order to deepen the existing knowledge concerning solvents and to recommend those most suitable for use in the performance of particular, uniform electrophilic attacks on copolymers. More especially three different modifications were examined at greater length in the course of this work, viz. sulfonation, chloromethylation, and nitration. Mechanistic aspects of these reactions, which are relatively simple and already well known with respect to their effects on monomers, had to be re-examined and carefully modified for the special requirements of the styrene-divinylbenzene copolymers.

In what follows, the subjects dealt with are described in greater detail.

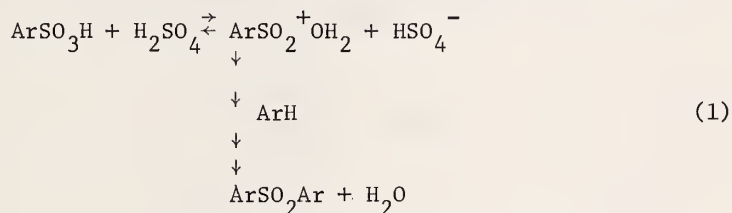
Swelling. The intrusion of non-polar organic solvents, such as methylene chloride, trichloroethylene, or tetrahydrofuran, cause a noticeable swelling of the network. The diffusing molecules generate an internal pressure in the polymeric chains, and these in turn are forced to swell. The process can be followed experimentally on a single copolymer bead by observing, under a microscope, the advance of a sharply defined "solvent front". Experiments of this type are a source of much fundamental information.

Many photomicrographs were taken for different non-polar solvents and one of the findings was that the depth of penetration progresses linearly with time. When the results were interpreted, with the aid of Fick's diffusion equation, it was found that the diffusion coefficient in these cases is dependent on positional coordinates.

Sulfonation. The kinetics of the sulfonation of styrene-divinylbenzene copolymers were investigated in the ternary system: methylene chloride - nitromethane - oleum, the first being the agent responsible for causing the copolymer to swell, the second a small penetrant molecule which forms an adduct with SO_3 , and the third a sulfonating agent. All the experiments, their results, and their interpretation were summarized in a paper (1). Experimental data in this paper point the way to the preparation of sulfonated ion exchange microstandards capable, within given limits, of adsorbing any predetermined amount of cationic species.

The maximum capacity achieved in this work was 4.66 meq./g, which is somewhat lower than the theoretical value (4.76 meq./g). The reason for the discrepancy is to be found in the nature of the copolymer, which consists of styrene molecules crosslinked with divinylbenzene. DVB is not, as a rule, very pure, but contains all three isomers (ortho, meta, and para); whereas the ortho and para isomers are easily sulfonated, this is not so with meta DVB.

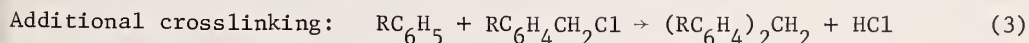
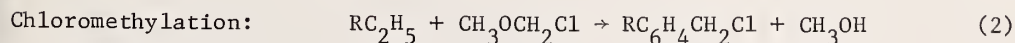
Another point of interest is the possibility of oversulfonation, i.e. the formation of sulfone bridges:



The existence of such sulfone bridges can be identified in the I.R. spectra of the sulfonated resins from the sharp asymmetric stretching vibration at 1380 cm^{-1} . It was proved in this work that, thanks to the mild sulfonation conditions used, this peak does not appear in the spectrum. Sulfone bridges are formed when more aggressive sulfonation agents are employed, e.g. chlorosulfonic acid with a Friedel-Crafts catalyst.

Chloromethylation. Copolymer chloromethylation is one of the more important processes, since the resulting product serves as the starting material for a wide variety of ion exchange and chelating resins.

In order to introduce a chloromethyl group into the aromatic rings of the copolymer, chloromethyl methyl ether with a Friedel-Crafts catalyst is used. In the ensuing process two reactions occur simultaneously:

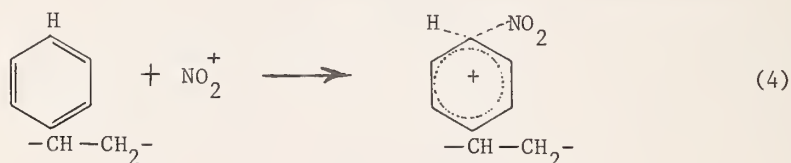


The main difficulties to be overcome are that (a) the methanol formed in reaction (2) tends to deactivate the Friedel-Crafts catalyst; (b) reaction (3) is an undesired side-reaction which increases the overall crosslinking of the copolymer and reduces the number of chloromethylated rings.

Many chloromethylation reactions involving different catalysts (AlCl_3 , SnCl_4 , and ZnCl_2) were carried out in the course of this investigation. It was found that ZnCl_2 is the best catalyst, not least because it reduces the undesirable side-reaction (3) to a minimum. The choice of the right solvent in this system also has a decisive effect, the more polar the solvent, the greater the extent of side-reaction (3). The quantity of catalyst added must therefore be carefully controlled, because reaction (3) tends to be promoted by excessive quantities of catalyst. The methanol formed in reaction (2) can be reacted with acetic anhydride to form hemiacetal or with formaldehyde to form methylal.

The results achieved so far have yielded a product which contains 20% chlorine. Experiments have to be still further verified and refined in order to attain the maximum capacity of the mono-chloro derivative, which should finally have a chlorine content of 22-23%, depending on crosslinking.

Nitration. Nitration is a straightforward associative electrophilic substitution process, in which NO_2^+ is the electrophile. The rate-determining step for this reaction is



NO_2^+ is not as strong an electron-withdrawing electrophile as SO_3 , so that the introduction of a second nitro-group into the aromatic ring is relatively easy. However, experiments and conditions had to be carefully worked out to ensure that a pure-nitro derivative (9.4% N) and a pure di-nitro derivative (14.4%) were obtained. The di-nitro derivative is of special interest, because it opens up the possibility of producing high-capacity ion exchange resins.

The monitor, Dr. Freeman, states:

The Schmuckler PL-480 project has been a stimulating source of progress in areas that are consistently complementary to our own work. Dr. Schmuckler has undertaken studies of aromatic sulfonation that have demonstrated better yield than we have been able to obtain at the NBS. The result was published, and it included a study of the applicability of an empirically useful and theoretically acceptable model for sulfonation kinetics that represents a significant step forward. A study of diffusion of solvent into copolystyrene/divinylbenzene networks has been undertaken and we have a difference in view point as to the extent to which it succeeded. This sort of debate is of high caliber and has a happy aspect of two groups being able to work together and yet think independently. Some good should come of it. The

most recent gain was an investigation of crosslinking phenomena during aromatic chloromethylation reactions. The results are definitive in determining what catalysts are acceptable to our needs, and which are not.

The idea of having a cooperative project activity in Israel has been rewarding all the way around and I am happy to report my definite satisfaction with the progress made.

Future Plans

The investigation of the chloromethylation process must be completed to the fullest extent possible, the end-result worked for being a product that has not undergone additional crosslinking. This product may subsequently be made to undergo further conversions with amines, phosphines, or sulfines, thus yielding a variety of anion exchangers in a wide range of selectivities.

After pure mono-nitro derivatives have been obtained, they can be subjected to a reduction process, resulting in the amines suitable for serving as starting materials for a whole range of new resins.

List of Publications that Resulted from the Project

1. D. H. Freeman, S. Goldstein and G. Schmuckler, Homogeneous sulfonation of styrene-DVB copolymers with oleum in organic solvents. Israel J. Chem. 7, 741 (1969).

A. 6. Standard Reference Materials Program

Project Title: PURIFICATION AND SINGLE CRYSTAL GROWTH OF SOME INTERMETALLIC COMPOUNDS BY THE ELECTRON-BEAM FLOATING-ZONE (EBFZ) METHOD

Principal Investigators: Dr. David Shaltiel and Dr. Moshe Oron

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. L. H. Bennett

NBS Institute or Center and Division: Institute for Materials Research
Metallurgy Division

Summary Description of Project Goals

Several intermetallic compounds, among them: UPd_3 , UFe_2 , ZrFe_2 , LaRu_2 , LaNi_5 and V_3Si will be purified by the Electron-Beam Floating Zone method. Growth of single crystals from all or part of the above or related compounds will be attempted by the same method. Physical properties to be investigated are: (i) magnetic susceptibility (bulk, MNR, Mossbauer, neutron diffraction), (ii) Fermi surface (de-Haas van Alphen effect, cyclotron resonance, positron annihilation), (iii) conductivity, (iv) magnetoresistance, and (v) superconductivity.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

A.7. RESEARCH TO IMPROVE PHYSICAL MEASUREMENTS

A.7. Research to Improve Physical Measurements

Project Title: DEVELOPMENT AND APPLICATION OF A 50 KeV FIELD-ION MICROSCOPE

Principal Investigator: Professor D.G. Brandon

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. Allan J. Melmed

NBS Institute or Center and Division: Institute for Materials Research
Metallurgy Division

Summary Description of Project Goals

It is proposed to construct a versatile 50 KeV field-ion microscope for structural investigations which will be suitable for imaging specimens of non-refractory metals and alloys of tip radius of the order of 1μ with a resolution of about 5 \AA .

Results and Implications to Date

The project monitor writes:

"Professor D.G. Brandon of the Technion-Israel Institute of Technology visited my laboratory for two weeks from August 30 to September 10, 1971, as part of the scientific relationship supported by the PL-480 program.... This visit was immensely worthwhile from both Professor Brandon's and my viewpoints.

During the visit we worked out the experimental details of an improved color superposition technique for field-ion microscopy (FIM) and used the technique to obtain unique data for the determination of the atomic structure of a dislocation core in tungsten. Professor Brandon is presently analyzing this data at the Technion. We made successful initial attempts at FIM imaging of a aluminum and titanium and began some tantalum anodizing experiments. The latter work directly stimulated an experimental project, within our OSW research program, which is currently being further pursued. Professor Brandon also made a suggestion towards the solution of a serious problem we were having with the image - amplifying element in our FIM. This suggestion was followed shortly after Professor Brandon left, and resulted in the complete elimination of the problem - saving possibly large expenditures of our time and money."

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

A.7. Research to Improve Physical Measurements

Project Title: DISSOCIATIVE ELECTRON CAPTURE AND ELECTRON TRANSFER REACTIONS OF
POLYATOMIC MOLECULES

Principal Investigator: Dr. Chava Lifshitz

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. Vernon H. Dibeler

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

The research program investigates dissociative electron capture processes which proceed via metastable temporary negative ion states, $[A^-]^*$, and electron transfer reactions from such temporary negative ion states to small molecules; e.g. NO_2 . Several classes of molecules exhibiting temporary negative states; e.g. halocarbons, aromatic polycyclics will be investigated.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

Project Title: STUDIES IN ENDOR SPECTRA IN INORGANIC CRYSTALS

Principal Investigator: W. Low

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. A. D. Franklin

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

Endor spectrum measurements on CaF_2 crystals containing rare earth ions (Yb^{3+} , Tm^{3+} , Ce^{3+} , Nd^{3+}) have been used to obtain the displacements of F^- ions in the vicinity of the trivalent ions on Ca^{2+} sites, both cubic (isolated) and tetragonal (with nearby F^- or H^- interstitials). A measure of covalency in the rare earth $-\text{F}^+$ bonding was also obtained. The present study will extend this work in 3 ways:

1. Examination of the change in displacements and covalency in the same fluorite lattice (probably CaF_2) as the rare earth ion changes from Ce to Yb through the lanthanide series.
2. Comparison of the overlap of the rare earth wave function on the fluorine ions with a given rare earth in the series CaF_2 , SrF_2 , and BaF_2 . The change in lattice parameter will afford the chance to examine the overlap as a function of interionic distance.
3. Comparison of isoelectronic divalent and trivalent rare earth ions in a given fluorite.

Results and Implications to Date

A new experimental technique, developed under this project, tentatively called the INDIRECT ENDOR EFFECT by Dr. Low is described by him as follows:

"We are saturating electron spin resonance transition, for example the uranium ion in single crystals of SrF_2 . We next observe the NMR solution of the fluorine by means of the ENDOR experiment. Let us for a moment assume that we observe F^- No. 1, (see Figure 1), that is to say the interstitial F^- . In this particular case, this frequency is in the neighborhood of 21 MHz if the magnetic field is directed along the 100 direction. Next adjust the NMR frequency so that you are sitting on the top of this ENDOR line. You begin to saturate this line. Now apply a second RF frequency and search for the NMR line of a F^- No. 2 or F^- No. 3. While sitting on F^- No. 1 you modulate the amplitude of the NMR No. 1 frequency. You sweep the second frequency and detect precisely at the modulation frequency of the first NMR frequency. As you sweep through the appropriate frequencies of the F^- No. 1 or No. 3, suddenly a signal appears with the opposite phase of that of the

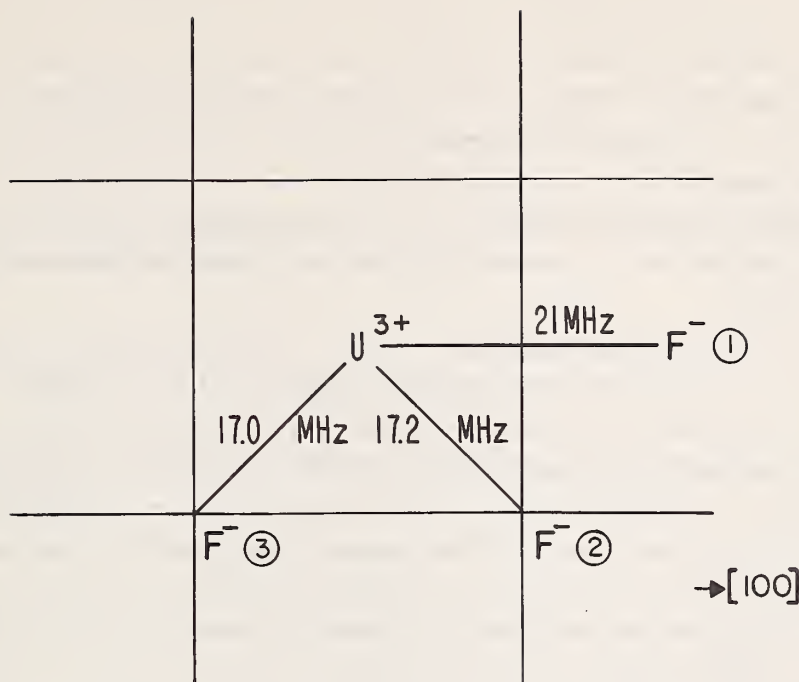


Figure 1. Displacements of ions neighboring a substitutional trivalent cation in fluorite.

first frequency. The inverse experiment has also been carried out. You sit on frequency No. 2 or No. 3., modulate its amplitude and sweep through the various frequencies and all other fluorine ions such as No. 1.

The tentative explanation of this effect is as follows:

Uranium wave functions extend selectively over the first shell of the fluorine ions. Modulation of the fluorine NMR frequency, therefore, is an indirect modulation of the uranium ion. This, in turn, modulates the F^- No. 2 and F^- No. 3 NMR frequency. Hence, the ratio of the intensities of the ordinary NMR frequency to that of the indirect ENDOR frequency which give the matrix elements connected with the covalent bonding of the second fluorine with the uranium ion. Very recent experiments, only two days old, have shown that there is a frequency shift of the order of 5-10 kilocycles, of the second NMR frequency, compared to a direct measurement of an ENDOR frequency of the second or third fluorine.

We think this whole field is very exciting and hope to publish soon in Physical Review Letters. The experiments were performed basically by Dr. E. Secemski and myself."

The project context within which this work is placed can be understood with the help of the following description of the problem and report of earlier results.

The purpose of this research is twofold.

1. To understand better the nature of the magnetic properties of rare earth ions in these crystals and, in particular, to plot out the extent of the wave function on the surroundings.
2. To explore with this method of Endor (electron nuclear double resonance) the distortion set up by the foreign ion in these crystal lattices. We shall briefly report here on the second problem.

Even perfect crystals have impurities. Many of these impurities are substitutional, that is to say they take the place of either a cation or anion in inorganic crystals. Sometimes these impurities have different valence states than the cation or the anion. It is expected that in these cases such a foreign ion will distort the immediate neighborhood around its location. Conventional macroscopic or microscopic techniques cannot at present detect the nature of this distortion. One does not know, therefore, whether such a distortion extends to the first shell, the second shell or the third shell of neighbours and to what an extent the crystal relaxes to take up a foreign ion with the wrong size and the wrong valence states.

An additional problem exists if the substitutional ion with excess or deficient charge may have a charge compensating ion or hole in the immediate neighborhood. Again, this will result in some rearrangement of the nearest and further lying neighbors around this complex.

The alkaline earth fluorides, such as calcium fluoride, are ideal hosts to investigate this problem. The rare earth ions are a nearly ideal probe to investigate relative rearrangements of these fluorines in this lattice. The reason for this is that the wave function of the rare earth ion does not extend very far on to the neighbors and, therefore, could be considered as an approximation to a point probe.

Within this framework we investigate two problems:

- (1) We compare the spectra of divalent and trivalent rare earth isoelectronic ions. For instance divalent thulium, trivalent ytterbium - both ions can be substituted for calcium ion at a cubic site and have a f^{13} configuration. We then find out to what extent does a trivalent charge distort the first and second shell by pulling in the fluorine ions towards the ytterbium ion.
- (2) We investigate the distortion around a rare earth ion if, in the next cube, there is a charge compensating ion located interstitially, such as an extra fluorine ion or hydrogen ion. We can plot out in this case the distortion of the next nearest (n.n.) neighbors fluorine ions and obtain a reasonable approximation for the distortion of the nearest neighbors of this rare earth complex. An interesting by-product is

that by comparing the spectra for two different interstitials, such as a fluorine ion and a hydrogen ion, we can receive considerable information regarding the interaction between rare earth ions and interstitial ions. This is particularly simple for the hydrogen ion interstitials, since this is a closed $1s^2$ shell.

We have so far obtained spectra for trivalent cerium, trivalent neodymium and trivalent ytterbium. We are now plotting out the spectrum of trivalent uranium. This last spectrum is far more complex since the uranium ion has a more extended wave function than the rare earth ions.

List of Publications that Resulted from the Project

1. D. Gill, M. Hayek, Y. Alon and A. Simievic, High Level NQR Spectrometer, Rev. Sci. Instr. 38, 1588, (1967).
2. D. Gill and D. Shaltiel, Calorimetric Detection of NMR in Ferro-Magnets, J. Appl. Phys., 38, 765, (1967).
3. D. Kiro, W. Low and A. Kafri, Comparison of Electron-Nuclear Double Resonance Spectra of $Ce^{3+}_H^-$ and $Ce^{3+}_F^-$ in Calcium Fluoride, Phys. Rev. Lett. 22, 893, (1969).
4. D. Kiro and W. Low, Distortion of the CaF_2 Ce^{3+} Lattice Caused by F^- and H^- Interstitials, Phys. Lett. 29A, 537, (1969).
5. D. Kiro, W. Low and D. J. Schipper, Endor of H^- and F^- Compensated Tetragonal Nd^{3+} Centres in CaF_2 , Phys. Lett. 29A, 586, (1969).
6. E. Secemski, D. Kiro, W. Low and D. J. Schipper, Comparison of Endor Spectra of $U^{3+}_F^-$ with $Nd^{3+}_F^-$ in Calcium Fluoride, Phys. Lett. 31A, 45, (1970).
7. D. Kiro and W. Low, Optical, Paramagnetic and Endor Spectra of Some Rare Earth Ions in CaF_2 , Int. Symp. on Electron and Nuclear Magnetic Resonance, Australia, 1969, Plenum Press, P. 247, (1970).
8. D. Kiro, W. Low and E. Secemski, The Structural Re-arrangement in CaF_2 Due to Trivalent Rare Earth Impurity Ions, Magnetism Conference, Grenoble (1970).

Project Title: STUDY OF THE MAGNETOELECTRIC EFFECT

Principal Investigators: Professor S. Shtrikman and Professor D. Treves

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. H. P. R. Frederikse

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

The purpose of this research is to get a better insight into the physics of how an electric field may influence magnetic properties as well as how a magnetic field can influence electric properties in insulating crystals like Cr_2O_3 .

For a more detailed consideration of the project goals we reproduce here the notes supplied by the principal investigators:

"In general, an interaction of electric or magnetic fields with matter presents itself as an electric and/or magnetic polarization of the medium. A magnetoelectric (ME) medium is one in which there exists a linear relationship between an electric field (E) and the induced magnetic polarization of the medium (M) and between a magnetic field (H) and the induced electric polarization (P). Such an effect is allowed in 18 ferromagnetic and 40 antiferromagnetic crystal classes and is expressed by the following tensorial relationship:

$$P_i = \chi_{ij}^{(m)} H_j \quad M_i = \chi_{ij}^{(e)} E_j$$

where, $\chi_{ij}^{(m)}$ and $\chi_{ij}^{(e)}$ are the magnetoelectric susceptibility matrices. The existence of the magnetoelectric effect (ME) was first predicted by Landau and Lifshitz⁽¹⁾ and then corroborated experimentally in a single crystal of Cr_2O_3 by Astrov⁽²⁾ and by Rado and Folen⁽³⁾. An extension of these studies was carried out by Shtrikman and Treves⁽⁴⁾ who first observed the ME effect in polycrystalline Cr_2O_3 after a suitable ME annealing in the simultaneous presence of magnetic and electric fields. This was later corroborated in other laboratories. Since the above observation the Department of Electronics at the Weizmann Institute of Science has been continuously engaged in theoretical and experimental studies of the ME effect. In particular the question of the origin of the ME effect in Cr_2O_3 was considered by a statistical mechanical study⁽⁵⁾ of its temperature dependence which is an elaboration of the approach used by Rado⁽⁶⁾. The importance of the shift as considered earlier⁽⁷⁾ was definitely proven in this study.⁽⁵⁾ An upper bound on the ME susceptibility which relates in a simple fashion the ME susceptibility to the magnetic and the electric susceptibility, was established.⁽⁸⁾

Recently, an apparatus enabling continuous recording of the ME effect as a function of temperature, from Liquid Helium up to above room temperature was constructed and successfully used in the first observation of the ME effect in FeSb_2O_4 (see

enclosure). With the same apparatus preliminary measurements of the critical behaviour in Cr_2O_3 were undertaken and an exponent of .36 defined by the relation $M (T-T_c)/T_c$ was found.

The purpose of this research project is to get a better insight into the physics of how an electric field may influence magnetic properties as well as how a magnetic field can influence electric properties in insulating crystals. This is of great importance to the determination of magnetic symmetry and spin structures⁽⁹⁾ as well as for the understanding of the statistical mechanics of the phase transition of some compounds. Apart from the basic interest in this work it is believed that if its goals are achieved it will contribute considerably towards the realization of devices based on the ME effects such as gyrators and memory elements.⁽¹⁰⁾

Our research plan is as follows:

(a) One expects that the ME effect should enable the determination of its critical exponents extremely close to the transition temperature, T_c . Our preliminary experiments do in fact support this. Encouraged by this observation we plan to measure accurately the parallel as well as the perpendicular critical exponent in Cr_2O_3 , possibly as close as $T-T_c = 10^{-5} T_c$. We also intend to look at the critical behaviour of the magnetoelectric effect in other materials such as $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$, $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ and LiMnPO_4 .

(b) As part of our search for new ME compounds we will look for the effect in $\text{Ga}_2\text{FeAlO}_5$, Cr_2WO_6 , Cr_2TeO_6 , V_2WO_6 , FeCrWO_6 , TiMnO_3 and DyFeO_3 , all of which are expected, according to their magnetic symmetry to exhibit the ME effect.

(c) It was recently shown by Hornreich⁽¹¹⁾ that suitable measurements should almost in all cases enable the determination of the magnetic classes of the ME polycrystal materials. Preliminary calculations by us suggest that this should be possible if one measures the ME effect as a function of the angle between the electric and magnetic fields present during the annealing. We intend to calculate theoretically the expected angular dependence and compare it with experiments. The effect of the amplitudes of the fields, in the annealing process, on the measured ME susceptibility will also be studied experimentally and theoretically. For that, a special cryostat incorporating a superconducting coil that enables measurements down to at least 1°K will be constructed.

(d) Finally, we plan to look at the so called "second order ME effect". This effect presents a quadratic dependence of the medium's magnetization on the applied electric fields. It is clear that a material which exhibits such a quadratic dependence, e. g. of the form $M \propto E^2$, becomes useful for frequency doubling of an electromagnetic radiation.

References

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5. R. Hornreich and S. Shtrikman, Phys. Rev. 161, 506 (1967).
6. G. T. Rado, Phys. Rev. 128, 2546 (1962).
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8. W.F. Brown, Jr., R.M. Hornreich and S. Shtrikman, Phys. Rev. 168, 574 (1968).
9. R. R. Birss, Symmetry and Magnetism (North Holland Publishing Co.) (1964).
10. T. H. O'Dell, Electronics and Power, p. 266 (1965).
11. R. M. Hornreich, private communication."

Results and Implications to Date

In a recent communication one of the principal investigators has told the NBS monitor:

"Since approximately six months have passed since the N.B.S. began its support of our research program on the magnetoelectric effect, we thought this would be an opportune time to bring you and your colleagues up to date on our activities and future plans.

1. New magnetoelectric materials; Besides $\text{Nb}_2\text{Co}_4\text{O}_9$, which we mentioned in our last letter to you, we have confirmed the existence of the magnetoelectric effect in four additional materials: $\text{Nb}_2\text{Mn}_4\text{O}_9$, $\text{Ta}_2\text{Co}_4\text{O}_9$, $\text{Ta}_2\text{Mn}_4\text{O}_9$, and Fe_2TeO_6 . The first three of these belong to the same family of transition metal niobates and tantalates as $\text{Nb}_2\text{Co}_4\text{O}_9$ and this confirms our expectation that this entire group of materials would be magnetoelectric. We hope to succeed in synthesizing the other members of the group (i.e. those containing Fe or Ni) shortly and to measure their magnetoelectric properties also.

The final compound, Fe_2TeO_6 , is a trirutile and belongs to an entirely different crystal structure than any presently known magnetoelectric material. We plan to examine other materials having such a structure (e.g. Cr_2TeO_6 , Cr_2WO_6) shortly. As regards publication, we have submitted an abstract, of which a copy is enclosed, of our results to date to the Annual Solid State Physics Conference to be held in Manchester, England, in January 1972. Two articles, one on Fe_2TeO_6 and the other on the $\text{Nb}_2\text{Co}_4\text{O}_9$ family of materials, are currently in preparation.

2. Annealing studies: Calculations of the magnetoelectric susceptibility as a function of the angle between the electric and magnetic fields present during the annealing process have been completed for the case of a polycrystal composed of randomly oriented crystallites having the non-zero tensor elements: $\alpha_{11}=\alpha_{22}$; α_{33} . This is the case for Cr_2O_3 as well as all the new magnetoelectric materials discovered by us to date. Experiments are being performed on Fe_2TeO_6 and an analysis of the results will be begun shortly.

3. Studies below 4.2°K : The equipment we have designed and built for this purpose is now in the final stages of testing. We intend to begin work in this particular area by

studying DyFeO_3 and GdVO_4 , both of which should be magnetoelectric below temperatures of 3.5 and 2.5°K respectively. If everything is satisfactory, we shall try and look at the critical behavior of the magnetoelectric susceptibilities in these materials. Single crystals of this material are available to us, so material preparation will present no problem.

Generally speaking, we feel that the program has been progressing satisfactorily and that the future prospects look very promising indeed."

In addition a publication has already resulted from this project (see reference below). The abstract reads as follows, under the title of "Some New Magnetoelectric Compounds":

"Since its initial discovery in Cr_2O_3 a decade ago, the magnetoelectric (ME) effect has been found to occur in a further dozen materials. By classifying ordered magnetic solids according to their magnetic space groups, additional compounds that are potentially ME have been identified. Powder specimens of these materials were prepared and pressed into pellets approximately 2.5 mm in width and 6 mm in diameter. They were then cooled to 4.2°K in the presence of either parallel or perpendicular electric and magnetic fields of approximately 10^6 v/m and 9 kg respectively. This is necessary in order to induce a remnant state in an antiferromagnetic material.⁽¹⁾ To measure the electrically induced ME effect, an alternating electric field was applied to the specimen and the induced magnetic moment was measured by an external pair of pickup coils as a function of increasing temperature.

Five new ME materials have been found. They are (with T_N in parentheses): Fe_2TeO_6 (210°K), $\text{Nb}_2\text{Co}_4\text{O}_9$ (27°K), $\text{Nb}_2\text{Mn}_4\text{O}_9$ (108°K), $\text{Ta}_2\text{Co}_4\text{O}_9$ (21°K), and $\text{Ta}_2\text{Mn}_4\text{O}_9$ (104°K). All have ME susceptibility tensors of the form $\alpha_{11}=\alpha_{22}$; α_{33} with all other elements zero. The two compounds containing Co had by far the largest ME susceptibilities. Possible explanations of this fact, a summary of the results obtained to date, and suggestions for further studies in this area will be presented.

(1) S. Shtrikman and D. Treves, Phys. Rev. 130, 986 (1963)."

In a second paper the authors give credit to this NBS project, although the work was really completed even before this project was officially activated. The abstract of this earlier paper (see second reference under the heading of "List of Publications that Resulted from the Project"), entitled "The Magnetoelectric Effect in $\text{Nb}_2\text{Co}_4\text{O}_9$ ", reads as follows:

"The niobate $\text{Nb}_2\text{Co}_4\text{O}_9$ was first synthesized by Bertaut et al.⁽¹⁾ It was found to crystallize in space group $\text{P}\bar{3}\text{c}1$ and to order antiferromagnetically at approximately 30°K with the spins forming chains parallel and antiparallel to the c axis. These results indicate that the magnetic point group of $\text{Nb}_2\text{Co}_4\text{O}_9$ should be $\bar{3}'m'$ and that this material should therefore exhibit magnetoelectricity. Powder specimens of $\text{Nb}_2\text{Co}_4\text{O}_9$ were prepared and pressed into pellets approximately 2.5 mm in width and 6 mm in diameter. A specimen was then cooled to 4.2°K in the presence of parallel electric and magnetic fields of approximately 5000 V/cm and 8000 g respectively. This is necessary in order to induce a remnant state in an antiferromagnetic material.⁽²⁾ To measure the electrically induced magnetoelectric (ME) effect, an alternating electric field was

applied to the specimen and the induced magnetic moment was measured by an external pair of pick-up coils.

The material was found to be ME for $T < 24^{\circ}\text{K}$, indicating that $T_N \approx 24^{\circ}\text{K}$. This was confirmed by powder susceptibility measurements. The ME susceptibility increased monotonically as the temperature was lowered and was essentially constant for $T < 10^{\circ}\text{K}$. The magnitude of the low temperature ME susceptibility following the anneal described above was of the same order of magnitude as that measured in Cr_2O_3 .⁽²⁾ The existence of a non-zero ME effect after a parallel annealing treatment confirms that the magnetic point group of maximum symmetry for $\text{Nb}_2\text{Co}_4\text{O}_9$ is indeed $\bar{3}'m'$.⁽³⁾

- (1) E.F. Bertaut, L. Corliss, F. Forrat, R. Aleonard, and R. Pauthenet, J. Phys. Chem. Solids 21, 234 (1961).
- (2) S. Shtrikman and D. Treves, Phys. Rev. 130, 986 (1963).
- (3) R. Hornreich, J. Appl. Phys. 41, 950 (1970)."

List of Publications that Resulted from the Project

1. "The Magnetoelectric Effect in $\text{Nb}_2\text{Co}_4\text{O}_9$ ", E. Fischer, R. Hornreich and D. Ignier, Bull. Israel Physical Society, 1971, pg. 29.
2. "Some New Magnetoelectric Compounds", E. Fischer and R. Hornreich, to be presented at the 9th Annual Solid State Physics Conference, Manchester, England, January 1972.
3. "The Magnetoelectric Effect - Materials, Physical Aspects, and Possible Applications", R. Hornreich, Invited talk to be presented at the International Conference on Magnetism (INTERMAG) Kyoto, Japan, April 1972, to be published in the IEEE Transactions on Magnetism.

A.8. RESEARCH TO IMPROVE MEASUREMENTS ON MATERIALS

A.8. Research to Improve Measurements on Materials

Project Title: CALCULATION OF ATOMIC TRANSITION PROBABILITIES

Principal Investigator: Professor M. Cohen

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. A.W. Weiss

NBS Institute or Center and Division: Institute for Basic Standards
Optical Physics Division

Summary Description of Project Goals

The frozen core approximation has proven successful for atoms with relatively simple cores. This research will investigate the possibility of extending this approximation to more complex atoms and will produce f-values for some selected first and second row atoms. Studies will also be undertaken to attempt to establish rigorous bounds on calculated f-values.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

Project Title: INFRARED STUDIES OF ADSORBED MOLECULES

Principal Investigator: Professor M. Folman, Dr. Y. Kozirvoski

Institution: Technion Research and Development Foundation, Ltd.

NBS Monitor: Dr. Marilyn Jacox

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

The infrared absorption and reflection spectra of molecules adsorbed on high surface area films will be studied. Measurements will be made on I.R. spectra of simple molecules such as NO, COS, HCl, adsorbed on high surface area of films of alkali halides. Due to high transparency of these films to I.R. radiation, spectra will be recorded in regions not usually explored in case of adsorbed molecules. Conclusions will be drawn about the existence of rotational freedom of movement of the adsorbate and preferred orientation of the adsorbate on the surface. Correlations will be made with the polarity of the adsorbate itself and with the lattice parameters of the underlying substrate. Using an I.R. interferometer, the investigations will be extended to the far infrared region, where vibrational degrees of movement of the whole molecule with respect to the adsorbent's surface may be observed.

Results and Implications to Date

Application of infrared spectroscopy to surface chemistry, especially in investigations of molecular adsorption on solid surfaces of catalytic importance is now recognized as a very valuable technique. It has been the subject of a large number of scientific papers, detailed reviews and recently of two monographs.

The adsorption spectra (in a very few instances also reflection spectra were recorded) have usually been compared with the known absorptions of the adsorbate in the gas, liquid and solid phases. Conclusions have been drawn from the shape of the absorption bands, shift in frequency and their intensities, about the chemical and physical properties of the adsorbate, type of surface bonding and surface site, orientation of the adsorbate and possible changes in its structure.

In recent years a method has been developed and employed in our laboratory¹ in which high surface area alkali halide films serve as adsorbents. This method completely overcomes the problems of transparency of the adsorbent over very wide spectral regions, and the difficulties arising from surface heterogeneity are very markedly diminished. The adsorbate films are prepared in situ in a low temperature infrared absorption cell. This cell differs essentially from the usual Dewars for spectroscopic work by including an additional compartment which serves as an adsorption cell. The high surface area films are deposited on a cooled window by evaporating a small alkali halide crystal from a tantalum furnace. Films so obtained have specific surface areas of the order of hundreds of square meters per gram and their transparency is excellent.

The important feature of spectra recorded for molecules adsorbed on these films is the

extreme sharpness and reproducibility of the absorption bands, hardly found in any of the known adsorption systems studied by infrared spectroscopy. This fact enables detection and resolution of absorption bands which are often only few wavenumbers apart.

An extensive study of the properties of evaporated alkali halide films (NaCl, NaBr, KCl, CsCl, CsBr, CsI) has been completed and gave much information about stability of these films, sintering conditions and extent of surface heterogeneity.

In the first stages of the research, spectra of HCN adsorbed on NaCl films were studied.¹ From the width and spectral shift of the ν_3 band conclusions were drawn regarding the binding of the adsorbate to the surface. The ν_1 band inactive in the gas phase was obtained. The ν_2 (the bending mode) appeared as a well resolved doublet indicating that the vibrational degeneracy was removed. Spectral shifts of the ν_3 mode were calculated using the quantum mechanical perturbation method. The calculated shift was in agreement with the experimental value.

Spectra of CO₂ adsorbed on NaCl, NaI, CsCl and CsF were studied extensively.² The ν_3 band appeared always as a narrow absorption not influenced by temperature which ruled out the existence of rotations in the system studied. The degenerate ν_2 mode appeared as a well separated doublet with components of equal intensity which indicated that in this case too the degeneracy was removed and the molecule was adsorbed parallel to the surface.

Another series of studies were carried out with N₂O₃ adsorbed on sodium³ and cesium⁴ halides. The most interesting feature of these spectra was the appearance of multiplets in spectral regions corresponding to the normal modes. These spectra were interpreted in terms of the existence of different adsorption sites on the surface.

Low temperature measurements (-196°C) were done with CO adsorbed on sodium halides.⁵ For NaCl adsorbent the heat of adsorption was calculated for various adsorption sites and orientations of the adsorbate. Agreement was found with experiment for molecules adsorbed perpendicularly on the surface of Na⁺ ions. Spectral shifts were calculated and good agreement with the experimental value was found. On CsCl films multiple absorptions were obtained indicating the existence of different adsorption sites.

The electrostatic potential outside ionic crystals plays an important part in calculating the energy of interaction between adsorbed molecules and the surface of such crystals. The contribution is most important when the adsorbate is a polar molecule with a substantial quadrupole moment. An analytical expression for the electrostatic potential and its derivative was given by Lennard Jones and Dent but only for the (100) face of the f.c.c. structure.

In our studies of molecules adsorbed on different alkali halides, we faced the problem of calculating heats of adsorption on b.c.c. structures exposing different faces. Analytical expressions for the potential and its derivatives outside (110) planes of f.c.c. and b.c.c. structures have been derived by means of Fourier analysis,⁶ and employed in calculations of adsorption heats and spectral shifts.

Induced infrared absorptions in H₂, HD and D₂ adsorbed on high surface area films of NaCl and CsI have been studied at 20°K. The frequencies of the induced absorptions were found to be shifted to lower values, compared to the gas-phase frequencies. The isosteric heat of adsorption of H₂ and NaCl was 1350 cal/mole, as found from isotherms recorded at

77°K and at 63°K. Adsorption potentials were calculated for different adsorption sites and orientations of H₂ on the 100 surface plane of NaCl. The relatively high heat of adsorption could be accounted for by a large contribution from quadrupole-field gradient interaction. Spectral shifts were also calculated, using the perturbation method and anharmonic wave functions of the adsorbate. Good agreement with the experimentally observed shift was found when the adsorption potential was employed as the perturbation and was expanded as a power series of the vibration coordinate.⁷

Infrared spectra have been obtained for NO adsorbed at different surface coverages on high-surface-area films of LiF, LiCl, LiBr, and LiI. These spectra have been interpreted in terms of dimers adsorbed on sites located in the surface planes and on the crystallite edges. Heats of adsorption have been calculated for single NO molecules having different adsorption sites and orientations and have been compared with the experimental values.⁸

References

1. Kozirovski Y. and Folman M., Infrared spectrum and spectral shifts of HCN adsorbed on evaporated alkali halides. Trans. Faraday Soc., 62, 808 (1966).
2. Kozirovski Y. and Folman M., Infrared spectra of CO₂ adsorbed on evaporated alkali halides. Trans. Faraday Soc., 62, 1431 (1966).
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4. Kozirovski Y. and Folman M., Infrared spectra of N₂O adsorbed on evaporated films of CsCl, CsBr and CsI. Israel J. Chem., 7, 595 (1969).
5. Gevirczman R., Kozirovski Y. and Folman M., Infrared spectra and spectral shifts of CO adsorbed on evaporated alkali halides. Trans. Faraday Soc., 65, 2206 (1969).
6. Gevirczman R. and Kozirovski Y., Electrostatic potentials outside ionic crystals. In press.
7. Folman, M. and Kozirovski, Y., Induced Infrared Absorption in H₂, D₂ and HD Adsorbed on High Surface Area NaCl and CsI. In press.
8. Lubezky, A. and Folman, M., Infrared Spectra and Dimerisation of NO Adsorbed on Lithium Halide Films. In press.

List of Publications that Resulted from the Project

R. Gevirczman and Y. Kozirovski, "Electrostatic Potentials Outside Ionic Crystals," in press.

M. Folman and Y. Kozirovski, "Induced Infrared Absorption in H₂, D₂ and HD Adsorbed on High Surface Area NaCl and CsI. In press.

A. Lubezky and M. Folman, "Infrared Spectra and Dimerisation of NO Adsorbed on Lithium Halide Films. In press.

Project Title: USE OF RESONANT CONVERSION ELECTRONS FOR THE STUDY OF SURFACE EFFECTS IN SOLIDS

Principal Investigator: Professor R. Fox and Dr. M. Ron

Institution: Technion - Israel Institute of Technology

NBS Monitor: Dr. J. R. DeVoe

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

Backscattered resonant conversion electrons will be used to study (a) the magnetic structure as a function of depth of bulk materials; (b) two-dimensional magnets and transitional magnetic properties of small particles and (c) local atomic environments of impurities.

Backscattered resonant conversion electrons (RCE) come from a maximum depth of several hundred angstroms. This can be compared with the effective depth of the associated 6.5 kev x-rays which is two to three orders of magnitude greater. The energy of the RCE emitted from the surface of the scatterer is equal to the incident energy (~8 kev) minus the energy loss in the solid which is proportional to the depth of origin. This will be exploited for studying surface properties of solids.

The proposed research will be carried out in the following stages:

- a) Construction of a high-efficiency energy-sensitive system for the detection of the backscattered RCE
- b) Energy calibration of the RCE as a function of depth of origin in various materials
- c) Study of
 - 1) the magnetic structure as a function of depth of
 - a) Bulk materials
 - b) Two dimensional magnets [thin films]
 - c) Transitional magnetic properties (superparamagnetisms-magnetism of small particles)
 - 2) crystal structure, elastic constants, electrical, magnetic, and chemical local atomic environment of penetrated impurities
- d) Possible technical applications: The RCE analysis can be used in a non-destructive manner for the investigation of
 - 1) Surface oxidation processes
 - 2) Surface hardening of iron and iron base alloys by
 - a) cementation and nitration
 - b) cold work
 - c) friction
 - 3) Coating [Analysis of the interface]
 - 4) Explosion welding and forming

Results and Implications to Date

A number of high efficiency energy dependent detectors for Resonant Conversion Mössbauer electrons have been built and are now being examined. The conversion electrons have the important feature of having their emergent energy dependent upon the thickness of the layer through which they passed which is several hundred angstroms.

After a satisfactory detector has been built, this feature will be exploited for studying interesting surface effects in solids. Many possible technical applications exist which have economic implications for Israel and the United States, as well as for the entire international community.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

A.8. Research to Improve Measurements on Materials

Project Title: THE DIRECT MEASUREMENT OF SMALL DIFFERENCES IN THE DIPOLE MOMENT AND POLARIZABILITY

Principal Investigator: E. A. Halevi, E. N. Haran, B. Ravid

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. A. A. Maryott

NBS Institute or Center and Division: Institute for Basic Standards
Electricity Division

Summary Description of Project Goals

An instrument will be developed for high precision measurements of dipole moment differences between isotopically related molecules.

Results and Implications to Date

This project was conceived some time ago when it became apparent that dipole moment differences between isotopic molecules might be related to secondary isotope effects on rates and equilibria. An approximate theoretical treatment for the estimation of isotope effects on dipole moment was worked out, and checked against the meager published experimental data then available.¹

An instrument was constructed which was designed to measure dielectric constant differences. The instrument measures the pressure dependence of the frequency ratio between twin LC oscillators, the capacitive cell of each of which contains one of the two gases. This measurement yields the ideal dielectric constant difference, and its repetition at a series of different temperatures allows the evaluation of the dipole moment difference and the difference in the temperature-independent part of the molar polarization, conventionally written as the sum of an "electronic" and an "atomic" polarization, ($P_E + P_A$).

The instrument was put into operation by B. Ravid, who established the validity of the method by measuring the dipole moment and ($P_E + P_A$) differences between two gases, HCl and HBr, the dielectric properties of which are well known. The complete description of the instrument and its operation have been published.² Even though the HCl-HBr measurements were carried out solely for calibration purposes, they yielded results of some interest: The measured value, $\mu(\text{HCl}) - \mu(\text{HBr}) = .284 \pm .002\text{D}$, agrees with the difference between the best published values of the dipole moments of the two molecules,³ but its precision is considerably better. ($P_E + P_A$) is larger by $2.40 \pm .05 \text{ cm}^3/\text{mole}$ in HBr than in HCl. The precision of this measurement goes well beyond that of previously available measurements by electrical means, and its agreement with the P_E difference, 2.36, derived from refractivity data,⁴ is theoretically significant.

The isotopic molecules, $\text{NH}_3 - \text{ND}_3$, were the first such pair studied. This investigation, the results of which are of considerable theoretical interest from several points of view, have been the subject of a preliminary communication⁵ but have so far been written up in full only in the form of a Ph.D. thesis.⁶ The results are:

$$\mu(\text{NH}_3) - \mu(\text{ND}_3) = -0.0156 \pm .0006 \text{ D}$$

$$(P_E + P_A)(\text{NH}_3) - (P_E + P_A)(\text{ND}_3) = 0.232 \pm 0.027 \text{ cm}^3/\text{mole}$$

Work with the instrument described above and with modifications of it has continued beyond the period of N.B.S. support and is still under way. Since isotopic dipole moment differences are now being obtained with high precision by rotational Stark effects and molecular beam methods, the future use of the present technique will probably be increasingly directed towards polarizability differences, and perhaps also towards isotope effects on polar properties in non-ideal systems, for both of which it appears to be eminently suited.

References

1. E. A. Halevi, Isotopic Polarity Differences, Trans. Faraday Soc., 54, 1441 (1958).
2. E. A. Halevi, E. N. Haran and B. Ravid, The Direct Measurement of Small Differences in Dipole Moment and Polarizability, Trans. Faraday Soc., in press.
3. R. D. Nelson, D. R. Lide, Jr. and A. A. Maryott, Selected Values of Electric Dipole Moments for Molecules in the Gas Phase, NSRDS-NBS 10 (1967).
4. A. A. Maryott and F. Buckley, Tables of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State, N.B.S. Circular No. 537 (1953).
5. E. A. Halevi, E. N. Haran and B. Ravid, Dipole Moment and Polarizability Differences Between NH_3 and ND_3 , Chem. Physics Letters, 1, 475 (1967).
6. B. Ravid, Ph.D. Thesis, Technion - I.I.T. (1968).

List of Publications that Resulted from the Project

E. A. Halevi, E. N. Haran, and B. Ravid, "The Direct Measurement of Small Differences in the Dipole Moment and Polarizability", Trans. Far. Soc. 67, 44 (1971).

Project Title: CHEMICAL AND CRYSTALLOGRAPHIC STUDY OF THE THERMAL DECOMPOSITION OF ALKALI-METAL PERMANGANATES

Principal Investigator: Professor F. H. Herbstein

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. Stanley Block (previously Dr. H. F. McMurdie)

NBS Institute or Center and Division: Institute for Materials Research
Crystallography Division

Summary Description of Project Goals

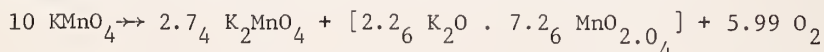
Our object was to determine the chemical equations describing the thermal decomposition of potassium permanganate in the temperature range 0-900°C. This goal was attained and the information obtained is now being applied to the study of

- (i) the industrial processes used for making KMnO_4 , which are nearly the obverse of those occurring in its thermal decomposition, and
- (ii) the nature of the poorly-crystalline " $\text{K}_4\text{Mn}_7\text{O}_{16}$ " phases produced in the thermal decomposition of KMnO_4 - these are of interest in the mineralogy and technology of manganese oxides.

The chemistry and kinetics of the thermal decomposition of KMnO_4 below 500°C have been studied by many workers but the chemical equations proposed for the reaction are many and varied. Our first purpose has been to determine the chemical equation describing the in situ thermal decomposition of KMnO_4 below 500°C. Our second purpose has been to obtain an overall picture of what happens when a sample of KMnO_4 is heated from 25-900°C. This has required study of the thermal behaviour of pure samples of K_2MnO_4 which decomposes above about 560°C to give, inter alia, K_3MnO_4 , which does not react further below 900°C.

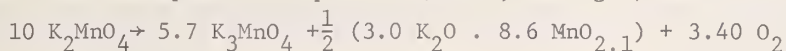
A major difficulty in this study has been the interaction of the primary decomposition products with carbon dioxide and water vapour of the ambient atmosphere, necessitating rather stringent drying and purification procedures. Concerted use of the techniques of TGA, DTA, X-ray diffraction and chemical analysis has simplified interpretation of the experimental results.

The decomposition equation (240°C, air) was found to be:



Decomposition in air at higher temperatures (up to 540°C) or in nitrogen gave the same amount of K_2MnO_4 but larger amounts of O_2 due to changes in composition of the " $\text{K}_4\text{Mn}_7\text{O}_{16}$ " phase (in brackets). This poorly-crystalline material rapidly absorbs water vapour from the atmosphere to form a poorly-crystalline hydrate " $\text{K}_4\text{Mn}_7\text{O}_6 \cdot n \text{ H}_2\text{O}$ " ($n \sim 5$); the hydrate dehydrates on heating above 100°C. " $\text{K}_4\text{Mn}_7\text{O}_{16}$ " and its hydrate have different (but unknown) crystal structures. The hydration and dehydration reactions are rapid and reversible.

Decomposition of K_2MnO_4 above $540^\circ C$ in air and nitrogen has been studied by the same techniques. The decomposition equation ($620^\circ C$, nitrogen) was found to be



This reaction was shown to be reversible in air. K_2MnO_4 reacts with atmospheric CO_2 to form unidentified phases at about $400^\circ C$ but these give the same decomposition products at higher temperatures as were obtained in a CO_2 -free atmosphere.

K_3MnO_4 was prepared separately and shown, by high-temperature X-ray diffraction, to undergo a number of phase changes on heating to $900^\circ C$; there is considerable hysteresis on cooling. K_3MnO_4 is stable in both dry air and nitrogen in the temperature range $25-900^\circ C$ but reacts rapidly with water vapour. The crystal structure of K_3MnO_4 is not known.

There is good agreement between our experimental results and most of the experimental results of earlier workers; there are, however, considerable differences in interpretation.

Similar but less detailed studies have been made for $RbMnO_4$, Rb_2MnO_4 and Rb_3MnO_4 , which are isomorphous with the analogous potassium compounds. The work is being continued, with particular emphasis on:

- (i) the crystallography of the " $K_4Mn_7O_{16}$ " phases. These phases are of interest in the mineralogy of manganese, as potential depolarizers in dry batteries and as possible examples of new types of defect structures in transition-metal oxide compounds.
- (ii) the solid-state reactions that occur between KOH and MnO_2 (or K_2CO_3 and Mn_2O_3) to give K_2MnO_4 . These reactions are important in the industrial manufacture of $KMnO_4$.

References

1. F. H. Herbstein, Crystallographic and Chemical Factors in Thermal Reactions of Solids, Isr. J. Chem., 7, 188 (1969).
2. F. H. Herbstein and L. D. Locker, Crystallographic and Chemical Study of the Products of Thermal Decomposition of Potassium Permanganate, Isr. J. Chem., 4, 1 (1966).
3. F. H. Herbstein and G. Ron, The Thermal Decomposition of Potassium Manganate, Isr. J. Chem., 7, 189 (1969).
4. F. H. Herbstein, G. Ron and A. Weissman, The Thermal Decomposition of Potassium Permanganate and Related Substances, Part I: Chemical Aspects, J. Chem. Soc. (A), p. 1821, 1971.

List of Publications that Resulted from the Project

1. F. H. Herbstein, G. Ron and A. Weissman, The Thermal Decomposition of Potassium Permanganate and Related Substances. Part I: Chemical Aspects, J. Chem. Soc. (A), p. 1821, 1971.

A.8. Research to Improve Measurements on Materials

Project Title: OXYGEN-17 HYPERFINE INTERACTION IN THE ESR SPECTRA OF OXYGEN CONTAINING FREE RADICALS

Principal Investigators: Dr. Zeev Luz and Dr. Brian L. Silver

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. R. L. Brown

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

The project aims are: to make a systematic ESR study of ^{17}O -hyperfine interactive constant in simple organic and inorganic oxygen containing free radicals trapped in solids; to analyze the experimental results in terms of the molecular structure and compare them with quantum mechanical calculations; and to provide a means for identification of radicals formed upon irradiation of solids.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

A.8. Research to Improve Measurements on Materials

Project Title: EXCITED STATE CHEMISTRY AND SPECTROSCOPY OF AROMATIC CHARGE TRANSFER COMPLEXES

Principal Investigator: Dr. Michael Ottolenghi

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. Richard A. Keller

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

Time resolved spectroscopic techniques will be used to study the excited states of charge transfer complexes. Special attention will be devoted to absorption spectroscopy of excited singlet and triplet states of the complexes leading to ionization and dissociation. A pulsed nitrogen laser will be used to study processes and lifetimes as short as 10 nanoseconds.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

A.8. Research to Improve Measurements on Materials

Project Title: IONIC ACTIVITIES IN MULTICOMPONENT SYSTEMS AND BIOLOGIC FLUIDS

Principal Investigator: Dr. J. Padova

Institution: Soreq Nuclear Research Centre

NBS Monitor: Dr. Richard A. Durst

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

Ionic activities will be measured in mixed electrolyte solutions of biological importance. The electrolyte activities will be measured by two independent techniques: (1) a gravimetric isopiestic method using an improved apparatus developed in this laboratory and (2) an electrometric method using ion-selective electrodes in cells without liquid junctions. Synthetic solutions of increasing complexity will be studied and activity data as well as medium effects measured. The activity data will ultimately be used in certifying standards for ions which are physiologically important.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

Project Title: THE STUDY OF UNIMOLECULAR DECOMPOSITION OF HALOALKYL RADICALS IN SOLUTIONS

Principal Investigator: Dr. L. A. Rajbenbach

Institution: Soreq Nuclear Research Centre

NBS Monitor: Dr. W. Braun

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

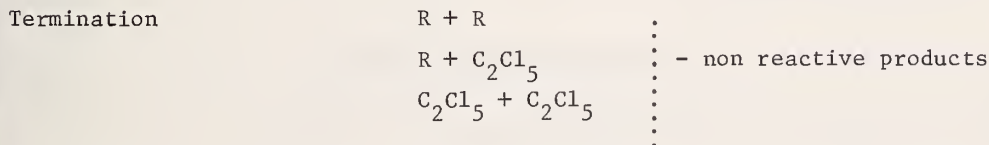
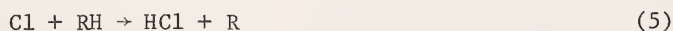
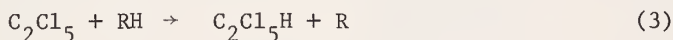
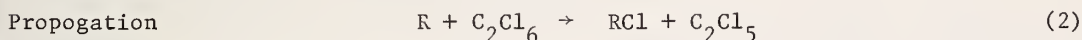
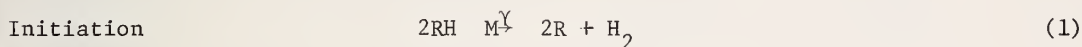
Summary Description of Project Goals

By radiolytic initiation of long chain reactions and by employing simple kinetic analysis, an evaluation of Arrhenius parameters at low temperatures of the decomposition of simple haloalkyl radicals in the liquid phase will be possible.

Results and Implications to Date

In describing this recently funded research, Dr. Rajbenbach writes:

In recently published work⁽¹⁾ we have reported the occurrence of gamma-radiation-induced free-radical chain decomposition of hexachloroethane in cyclohexane. The relevant reactions are (where RH denotes alkane solvent):



Steady-state treatment of reactions 1-5 leads to the following expressions:

$$G(\text{C}_2\text{Cl}_5\text{H}) = \frac{1}{1+k_4/k_3(\text{RH})} G(\text{RCl}) \quad \text{I}$$

$$G(\text{C}_2\text{Cl}_4) = \frac{1}{k_3(\text{RH})/k_4+1} G(\text{RCl}) \quad \text{II}$$

The plot of $\log \frac{G(C_2Cl_4)}{G(C_2Cl_5H)}$ as a function of $1/T$ enables us to obtain the ratio of $\log (A_4/A_3)$

and E_4-E_3 .

Thus radiolytic initiation of long chain reactions enables us to determine at a relatively low temperature range and by simple kinetic analysis the relevant Arrhenius parameters.

We are mainly interested in E_4 (by substituting known values of E_3). It should be mentioned that the activation energy values of unimolecular radical decompositions are very scarce (up to 50 rate constants have been determined so far - see J. A. Kerr and A. C. Lloyd, Quarterly Rev. 22, 549, 1968).

It seems reasonable to assume that in non-polar solvents E_4 values are quite close to those in the gas phase, under which conditions E_4 represents the C-Cl bond strength.

We intend to extend this work by studying the E_4-E_3 values for ethyl radicals containing four and three chlorine atoms, as well as for mixed halogen radicals, especially bromo-chloro and fluoro-chloro ethyl radicals.

In addition to the determination of E_4 values, we are interested in elucidating the nature of the halogen elimination step (reaction 4).

The inclusion of fluorine and bromine atoms in the solute molecule should enable us, at least qualitatively, to estimate the contribution of steric compression and electronic repulsion factors in the halogen elimination step.

Another aspect of this research would be the study of the effect of the polarity of the solvent (RH) on E_4-E_3 values. We think that in this part of the study, photochemical initiation may be preferable to the radiolytic one.

- 1) A. Horowitz and L. A. Rajbenbach
J. Phys. Chem. 74, 678-681 (1970)

For other closely related, recent work, see also:

- A. Horowitz and L. A. Rajbenbach
J. Amer. Chem. Soc. 90 4105-8 (1968)
ibid. 91 4626-31 (1969)
ibid. 91 4631-34 (1969)

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

A.8. Research to Improve Measurements on Materials

Project Title: ELECTRON-DENSITY DISTRIBUTION IN ATOMS AND BONDS OF ORGANIC MOLECULES

Principal Investigator: The late Professor G.M.J. Schmidt

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. Stanley Block

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

The anisotropic electron-density distribution around the row-two atoms, in particular C, N and O, and in the chemical bonds involving these atoms in various states of hybridization are to be studied by low temperature x-ray diffraction.

Results and Implications to Date

Dr. Schmidt describes this recently funded grant in the following manner:

1. We are continuing the study of anisotropic electron-density distribution around the row-two atoms, in particular C, N and O, and in the chemical bonds involving these atoms in various states of hybridization.

We consider this information to be of primary importance for the description of organic molecules (with or without the hetero-atoms nitrogen and oxygen) and for the eventual quantitative analysis of the chemical bonds in these molecules by the choice of appropriate wave functions.

We consider further that such information, in particular the electron-density distribution around multiple bonds ($C=C$ and $C\equiv C$) and the lone-pair distribution of the hetero-atoms, whether in the sp^3 or sp^2 states of hybridization, is largely responsible for molecular conformation (as the result of lone-pair interaction with polarisable atoms or groups such as halogen or the C-H bond, cf. the much debated C-H...O interaction; lone-pair...lone-pair repulsion) and for molecular packing arrangements in crystals or organic compounds.

2. It has been shown by several laboratories^{1,2} including our own³ that very accurate X-ray diffraction data are capable of yielding electron-density maps which reveal the details required for this study.

It is evident from these results that there remains the need for further technical improvement which has now become possible with the introduction of low-temperature X-ray diffractometry. We consider it particularly important to record sets of diffraction data at a series of temperatures in order to measure the thermal vibration parameters of molecules susceptible to rigid-body motion analysis as a function of temperature, and thereby to interpret the atomic vibration tensors in a physically meaningful way rather than accept them as computationally derived numbers from measurements at one temperature. Since much of the looked-for anisotropic bonding effects are buried in the anisotropic temperature factors their precise determination is an essential part of this proposal. Implied in this experimental improvement is the direct determination of the scale factor of the measured intensities by comparison against a well-defined standard, rather than by computational procedures.

3. It has been shown that the atomic co-ordinates obtained from X-ray data are subject to errors as the result of the non-inclusion in the scattering factors of aspherical electron-density distribution of the (generally assumed spherical) scatterer. This effect is known systematically to shorten the C-H bond length;⁴ we have recently shown that this shortening can amount to as much as 0.03 Å in the C=C and C≡N groups as a result of the localisation of electron-density in these triple bonds.³ In the absence of neutron-diffraction data (which locate nuclear position) we are developing computational procedures⁵ which attempt to remove the difficulties inherent in X-ray diffraction methods.

4. We consider it essential to choose particularly carefully the compounds for the type of detailed (and time-consuming) structure analyses proposed here. In a previous report to the NBS we enumerated as desirable conditions for this line of research:

- a. high melting point, low sublimation rate; hence minimal loss in weight of the specimen during measurements.
- b. stability to X-rays.
- c. chemical symmetry to permit statistical checks based on the internal consistency of the measured data.
- d. chemical interest.
- e. study of the same molecule in a variety of crystallographic and chemical environments.

5. It is now proposed to analyse compounds in which both bonding electron-density and intra- and inter-molecular effects, interrelated in the manner set out above, are simultaneous objects of study (objective d.). During the last year we have conducted preliminary work⁶ on complexes of dicarboxylic acids (e.g. oxalic, succinic acids) with primary amides (crotonamide, benzamide, furoamide) which also adequately fulfill conditions a. to c. The already available structural data indicate that condition d. is equally attainable in this series. The data which have recently become available for the electron-density distribution in (hydrogen-bonded) oxalic acid² can be matched against the results to be obtained here (condition e.). The packing structure of the complexes is determined by a fine balance, not yet completely understood, of attractive hydrogen-bonding and repulsive forces both critically controlled by lone-pair effects. Since the amide components can be chosen for their own intrinsic interest (C=O, C-N bonds, C=C double bond etc.) the amount of information to be gathered from such a project appears to us to be commensurate with the effort to be invested.

6. Equipment available includes standard X-ray equipment, an IBM 1800 controlled "Siemens" diffractometer and a "Nonius" diffractometer with low-temperature attachment. The interface to the IBM 1800 has been constructed. The computer programmes required for this project exist.

References

1. A. M. O'Connell, A. I. M. Rae and E. N. Maslen, Acta Cryst., 1966, 21, 208.
2. P. Coppens, T. M. Sabine, R. G. Delaplane and J. A. Ibers, Acta Cryst., 1969, B25, 2451.

3. A. Hartmann and F. L. Hirshfeld, Acta Cryst., 1966, 20, 80.
4. F. L. Hirshfeld and D. Rabinovich, Acta Cryst., 1967, 23, 989.
5. A. Jungk and G. M. J. Schmidt (unpublished).
6. C. M. Huang, M.Sc. Thesis, 1969, Feinberg Graduate School at the Weizmann Institute of Science.

Since writing these comments for the present NBS Technical Note Professor Schmidt has tragically succumbed to cancer. One paper published under this contract has however appeared with himself as co-author. Its abstract reads as follows:

"The electron-density sections in the planes of the benzene rings of penta-*m*-phenylene (PMP), hexa-*m*-phenylene (HMP), and 1:2,5:6,9:10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyn(TTT) have been computed and averaged as well as the sections parallel to the ring planes at a distance of 0.4 Å. The results demonstrate σ -density in the centres of the (aromatic) C-C bonds and π -density above the ring planes. Sections passing through the aromatic and exocyclic bonds of the three compounds have been averaged and show ' π ' density maxima at approximately 0.5 Å from their bond centres. The averaged electron-density distribution in the -C \equiv C-triple bond of TTT contains a trough of $-0.2 \text{ e}/\text{\AA}^3$ in the centre as well as ' π ' peak density of $0.1 \text{ e}/\text{\AA}^3$ at 0.6 Å distance from the centre of the bond. The anhydrous form of acetylenedicarboxylic acid (ADA) also exhibits a trough in the centre of its -C \equiv C- triple bond."

List of Publications that Resulted from the Project

1. "Studies in Bonding Electron Density. Part 1.", H. Irngartinger, L. Leiserowitz and G. M. J. Schmidt, J. Chem. Soc., Section B, Phys. Org. Chem. p. 497 (1970).

A.8. Research to Improve Physical Measurements

Project Title: PREPARATION OF SINGLE CRYSTAL METAL OXIDES BY CHEMICAL VAPOR TRANSPORT

Principal Investigator: Dr. M. Shiloh

Institution: Soreq Nuclear Research Centre

NBS Monitor: Dr. F.E. Brinckman

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

Development of techniques for single-crystal growth by chemical vapor transport (CVT) methods will be examined with emphasis on several classes of metal oxides. Among these are the important binary semiconductor ZnO, the ternary ferroelectric LiNbO_3 , and the ferri-magnetic garnets. The work will systematically evaluate growth conditions from the vapor, relating their sensitivity to various parameters; temperatures, pressure, concentration, type of transport reagent, geometry of the system, and type of substrate. In addition to characterization of product crystals by chemical and spectroscopic means, achievement of optimum growth conditions will permit assessment of the thermodynamic properties for systems where such data are presently unavailable.

Results and Implications to Date

The first results of this research were described in a paper delivered to the International Congress on Crystal Growth in Marseilles, France in July 1971. In that paper the authors, Dr. M. Shiloh and Dr. J. Goodman, described the evaluation of several transport agents for growing single crystals of zinc oxide in a closed system. The experimental results were compared with calculated thermodynamic quantities. Ammonia, hydrochloric acid, hydrogen and ammonium chloride were chosen for evaluation as transport agents. It was shown from thermodynamic data that of these ammonia should be the most effective transport agent and that hydrochloric acid should be a much poorer agent than both hydrogen and ammonia mainly because of the very small change in equilibrium constants with temperature. The same conclusion can also be reached by comparing the change in the number of moles for each reaction. The results should confirm the agreement between the relative value of calculated equilibrium partial pressure difference and the relative amount of transport of zinc oxide.

An interesting effect was observed when ammonium chloride was used as transport agent. When the source chamber temperature was raised from 100°C to 1075°C the transport rate decreased instead of increasing as was expected. After the ampule was opened it was observed that most of the powder source also changed into single crystals. By further thermodynamic analysis it became apparent that because of water produced in the reactions at a temperature of approximately 1000°C reversed transport of oxide from the lower temperature to the higher one should occur.

The crystals grown gave good X-ray diffraction panels corresponding to the structure of the original powdered sample. Spectrographic analysis showed the starting materials to have 10 parts per million of lead and 1 part per million of cadmium whereas the final single crystals grown in ammonium chloride showed less than 1 part per million of both these elements. The decontamination for cadmium is particularly remarkable because of its great chemical similarity with zinc.

In a later letter the principal investigator writes to the NBS monitor (quoted in part):

"I have already started transport experiments on Al_2O_3 in a closed system. Preliminary thermodynamic calculations show that the most promising transport agents should be niobium and tantalum pentachlorides and also a system containing a mixture of HgCl_2 and CS_2 . The first results are still under evaluation and a rigorous x-ray identification of the transported material has not been done yet, but chemical analysis results show that Al_2O_3 was indeed transported by NbCl_5 or the mixture $\text{HgCl}_2 + \text{CS}_2$. The transport systems of Al_2O_3 are much more complicated than those of ZnO and a clear understanding would be possible only by performing mass spectrometric experiments. ... I had the opportunity to talk with Dr. Peiser in his short visit in Soreq. He told me that people in NBS might be interested in making ESR or other measurements on the ZnO crystals that I have prepared. As I've told Dr. Peiser I'll be very glad to send sample crystals...."

At an even later stage the monitor reports that he has been able to grow single crystals of ZnO doped with transition metal elements, using mercuric chloride as transport agent.

List of Publications that Resulted from the Project

1. "Growth of ZnO Single Crystals by Chemical Vapour Transport", M. Shiloh and J. Gutman, paper delivered to the International Growth Congress, July 1971, to be published in International Journal of Crystal Growth.

A.8. Research to Improve Measurements on Materials

Project Title: MACROMOLECULES AT INTERFACES

Principal Investigator: Professor A. Silberberg

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. Robert R. Stromberg

NBS Institute or Center and Division: Institute for Materials Research
Polymers Division

Summary Description of Project Goals

The adsorption of polymers at interfaces will be studied theoretically and experimentally, with special emphasis on segment distribution.

Results and Implications to Date

In a recent communication relating to this newly funded grant, Dr. Silberberg has stated "The adsorption of macromolecules to interfaces presents a number of unusual features which have by now been well characterized and documented. In brief, macromolecules adsorb well at most interfaces and from solutions whose concentration may be very low indeed. The poorer the solvent the better is the adsorption, but over a wide range of concentrations the amount adsorbed and the internal structure of the adsorbed layer does not depend on the bulk concentration. For example, in the case of macromolecules, only a part of the segments establishes contact with the interface and this fraction, which generally runs between 0.25 and 0.4, does not vary with concentration in the plateau region. Adsorption increases with increase in molecular weight but above a certain molecular weight range no further improvements in adsorption are achieved.

A number of very interesting theoretical aspects are involved in the explanation of these effects and most of these have been well covered in the literature over the last decade. Comparison with the results of experiment are not always easy since parameters such as specific surface area and specific interaction free energy are not readily measured. Moreover these interactions are slow to get into equilibrium and only in the minority of cases has the establishment of equilibrium been uncontroversibly proven. Nevertheless the agreement between theory and experiment is substantial in the points cited so that there is every reason to feel confident about the interpretation.

A major point of disagreement remains, however. This arises in connection with the thickness of the adsorbed layer. Experimental results for these to date, on the whole, give values larger than would reasonably be anticipated. Our project is mainly concerned with this issue, to reconcile the discrepancies and to compare our understanding of the structural arrangements in macromolecular interfacial layers.

Macromolecular surface layers have many important functions both in technology and in biology. Some of these we understand reasonably well, others we can only guess at. We use these layers in making adhesives, in flocculation, in dispersion in making of composite materials and in effecting chromatographic separations. Layers of this kind occur at almost any biological interface and while their role in these cases has not been considered too generally in the past, their importance in modifying and modulating

mechanical and physico-chemical interactions between phases is now being more and more appreciated.

Basic to any of these problems are adequate theoretical and experimental tools to describe and measure the segment distribution at an interface. Optical and hydrodynamic techniques have been applied so far. Of these the latter has interesting direct implications in the interpretation of one of the most important function of these layers, the mechanical interaction. In order to relate hydrodynamic effects to structure we have to understand how layer structure influences flow and deformation at the interface. Hydrodynamic experiments and their interpretation thus go close to the heart of one of the most important aspects of these layers.

We have at our disposal now a very accurate hydrodynamic technique which can detect changes in effective layer thickness to within 10\AA . With this technique we have begun to measure the build up of the layer from very dilute solutions. It is our plan in the present project to continue to accumulate hydrodynamic data as a function of flow conditions on well characterized polymer-solvent systems in the dilute solution range and to compare these results with data obtained by optical means (ellipsometry) in the same systems. Techniques are being developed which will allow more detailed structural descriptions to be derived from the optical data. The compatibility of the optical and hydrodynamic data will be tested by examining flow at low shear rates and in the limit of zero flow rate.

The following features have already been shown by our flow measurements to characterize the adherence of long chain macromolecules (polystyrene) from very dilute solution (toluene or cyclohexane) onto glass:

1. With macromolecules of molecular weights in the usual range, the build up of the surface layer occurs at concentrations of the order of $10^{-8} - 10^{-7}$ g/ml of polymer.
2. The layer built up at these concentrations is relatively thin of the order 100 to 300 \AA thick.
3. In the concentration range $10^{-5} - 10^{-4}$ g/ml of polymer there is a renewed relatively sharp and very marked increase in adsorbed layer thickness. This increase then gives rise to the plateau, which persists over several decades of concentration, at the very high values usually observed.

It is clear that the first build up of a layer mentioned under (1) above refers to the gradual accumulation of macromolecules on the surface, first each in isolation and then gradually more and more of them until the layer is complete. Since with the flow technique we are able to follow this process with considerable precision we anticipate that, with some improvements, we shall be in a position to assess the form in which the isolated macromolecule is first adsorbed and then follow the structural changes which result from gradual interaction and interpenetration. One important point, for example, has already been demonstrated. From the dependence of these effects on the molecular weight of the polymers, it appears that the effective thickness of the layer undergoes a transition from dominance by the polymer tails to dominance by the polymer loops as the molecular weight is increased.

Existing theoretical models are to be re-examined in the light of these results."

List of Publications that Resulted from the Project

This project was funded too recently for there to have been any publications by this date.

A.8. Research to Improve Measurements on Materials

Project Title: STUDY OF BAND STRUCTURE BY THE DIFFERENTIAL OPTICAL METHODS

Principal Investigator: Y. Yacoby

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. A. Feldman

NBS Institute or Center and Division: Institute for Materials Research
Inorganic Materials Division

Summary Description of Project Goals

The band structures of Sc_2O_3 , TiO_2 , SrTiO_3 , V_2O_3 and V_2O_4 will be investigated with special reference to the 3d conduction band and the metal phase transition in V_2O_3 and V_2O_4 .

Results and Implications to Date

A. The electrical resistance of vanadium oxide (V_2O_3) changes from about $10^{-2}\Omega\text{cm}$ at room temperature to $10^4\Omega\text{cm}$ at liquid air temp. Thus one cannot make electro reflectance measurements either at room temperature because the resistivity is too low and metallic, or at low temperatures where the electrolyte method cannot be used. On the other hand, thermorefectance measurements can be performed throughout the whole range of temperatures. Moreover, thermorefectance measurement allows one to measure directly the effect of phase transitions on band structure.

The system for measuring thermorefectance may be divided into 4 parts:

- (a) Optics. This is an ordinary setup built of mirrors which image the light source on the sample and converge the reflected light on the entrance slit of the monochromator. Light at a selected wavelength is converged on the light detector.
- (b) Temperature control. The temperature of the sample can be varied from slightly above He temperatures up to room temperature. In addition, we can vary the temperature of our sample at a frequency of 1 Hz with an amplitude of about 15°C .
- (c) Detection system. The light from the light source is modulated by a mechanical chopper at 400 Hz. In addition, the amplitude of the reflected light is modulated at 1 Hz. This modulation is caused by the variation of the reflection coefficient with temperature. The electrical signal obtained from the light detector is first amplified with a band pass amplifier. The output is detected by a peak detector resulting in a signal with a component at 1 Hz. This signal is detected by a lock in detector which is in phase with the temperature variations of the sample.

(d) Control system. This is an automatic control which allows the system to perform many scans and to accumulate the information in a special purpose computer. With this system we are able to perform thermorefectance measurements on any crystal independent of its electrical resistivity in optical wavelengths between 0.2μ and 10μ . The minimum depth of modulation of the reflected light that can be detected in the infrared (4μ to 10μ) is about 1:5000 and in the ultra violet (0.2μ to 0.5μ) is about 1:100000. Thermorefectance measurements have been performed on V_2O_3 . The measurements in the spectral range between 0.2μ to 0.5μ were performed at room temperature. The results have as yet not been analyzed.

B. The interpretation of differential measurements is in many cases very difficult. Performance of these measurements under strong uniaxial stress may be of considerable help. Electro-reflectance measurements have been made by several authors under strong uniaxial strain but to date no electro-absorption measurements on thin crystals ($<200\mu$) have been carried out under strain.

We have developed a very simple method to perform such measurements: A thin sample (100μ) is glued by Eastman 910 glue on a 1 mm thick steel ribbon. Small holes are made in the steel to allow transmission of light through the sample. The sample is then bent in such a way that the crystal is depressed. The strain is measured by a strain gauge. Using this method we were able to obtain strains of 0.5% in crystals in $SrTiO_3$.

C. Results

1. The optical thermorefectance on V_2O_3 has been measured at room temperature over the photon energy range 0.5eV-5.8eV. The results have been analyzed in terms of presently available theory. These results are soon to be published.
2. Electroabsorption, thermorefection and the derivative of reflection with light frequency ($\frac{1}{R} \frac{dR}{d\omega}$) have been measured at room temperature in $SrTiO_3$. The electroabsorption has been measured below the absorption edge. The thermorefectance and $\frac{1}{R} \frac{dR}{d\omega}$ have been measured above the absorption edge up to 5.8eV. The results have been Kramers-Kronig converted and the spectra of $\frac{d\epsilon_2}{d\epsilon}$ and $\frac{d\epsilon_2}{dT}$ have been obtained. From a comparison of the two spectra, semiquantitative information on the change of energy gaps in the material with temperature have been obtained. Moreover, from a comparison of the two spectra one can identify the points in energy which correspond to critical points in the Brillouin Zone. Tentative assignments of the structure are proposed.

The work is of general importance because it will produce information concerning the energy band structure of a number of transition metal oxides that are receiving considerable attention these days. Both methods (electro-optical modulation and piezo-optical modulation) are presently being pursued in the Solid State Physics Section of the NBS. The crystals suggested by the principal investigator are somewhat complementary to the efforts in the Solid State Physics Section of the NBS.

List of Publications that Resulted from the Project

1. "Optical Thermoreflectance in V_2O_3 ", P. Shtorch and Y. Yacoby, Physics Letters, Vol. 36A Number 2, p. 89-90, August 16, 1971.

A.9. DETERMINATION OF DATA REQUIRED BY THE MEASUREMENT SYSTEM

A.9. Determination of Data Required by the Measurement System

Project Title: EXPERIMENTAL TEST OF THE CURRENT THEORY OF LIQUID METALS: THERMAL CONDUCTIVITY

Principal Investigator: Professor A. J. Greenfield

Institution: Bar-Ilan University

NBS Monitor: Dr. R. D. Mountain

NBS Institute or Center and Division: Institute for Basic Standards
Heat Division

Summary Description of Project Goals

A method for determining the thermal conductivity of liquid metals with high accuracy will be developed. The measurements are to be used as a sensitive test of current theories of the thermal conductivity of liquid metals. The method is based on a radiometric determination of the surface temperature of calibrated stainless steel tubes containing the metal. Conduction and convection losses are controlled by heating from the top of the tubes and by placing the tubes in an evacuated chamber.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

A.10. EXPLORATORY RESEARCH

A.10. Exploratory Research

Project Title: SPECIAL TOPICS IN MATHEMATICAL ANALYSIS OF INTEREST TO NBS

Principal Investigator: Professor S. Agmon

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. H. J. Oser

NBS Institute or Center and Division: Institute for Basic Standards
Applied Mathematics Division

Summary Description of Project Goals

Studies of the Schrodinger operator A with a general potential $q(x)$ are planned. For example, as an extension of earlier work it is proposed to find the most general conditions on the potential $q(x)$ which ensure that all self-adjoint realizations of A possess a purely continuous (positive) spectrum. In addition investigations will be conducted in the area of asymptotic formulas with remainder estimates for the eigenvalues of elliptic operators. Specifically, the problem of determining optimal remainder estimates will be considered. A detailed study is planned of the relations between absolute and commutative convergence in general linear topological spaces. Included will be the elucidation and extension of a unified principle which has been found to underlie constructions in Hilbert space which can be applied to arbitrary Banach spaces. Classical theorems on functions of complex variables will be extended to analytic functions in Banach spaces.

Studies will be conducted in ergodic theory of Markov processes. Among the proposed areas of interest are conditions for the existence of invariant measures and limit theorems for Markov processes.

Results and Implications to Date

In a progress report on this recently activated grant Dr. Agmon writes in part:

"I can say that I have developed a new method which enables a very precise investigation of the spectrum of Schrodinger operators. The method is based on a priori estimates. For very general potentials I have been able to show that the positive spectrum of a Schrodinger operator is absolutely continuous. The results improve well-known results by Ikebe and Kato."

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

A.10. Exploratory Research

Project Title: MOLECULAR THEORY OF FLUIDS

Principal Investigator: Dr. Shalom Baer

Institution: The Hebrew University of Jerusalem

NBS Monitor: Dr. Max Klein

NBS Institute or Center and Division: Institute for Basic Standards
Heat Division

Summary Description of Project Goals

A perturbation theory previously developed by the principal investigator will be very carefully studied, with the aim of developing a truly microscopic molecular theory of fluids. The perturbation theory is based on the treatment of a fluid as a system of electrons and nuclei. The structure of the perturbation expansion will be studied in the sense that the various kinds of diagrams which appear will be classified and attempts made at their summation. The theory does not depend on the assumption of model intermolecular potential functions. Instead, it could lead to an understanding of the behavior of the effective intermolecular potential functions in the fluid as a function of the thermodynamic parameters of the fluid. The perturbation theory is a very fundamental one and has broad and practical potential. A major emphasis in this work will be placed on the development of a molecular theory of very dense fluids.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

A.10. Exploratory Research

Project Title: DEVELOPMENT AND USE OF MULTI-CONFIGURATION SELF-CONSISTENT FIELD THEORY TO STUDY MOLECULAR DYNAMICAL PROCESSES

Principal Investigator: Dr. Harold Basch

Institution: Bar-Ilan University

NBS Monitor: Dr. M. Krauss

NBS Institute or Center and Division: Institute for Materials Research
Physical Chemistry Division

Summary Description of Project Goals

This study is an attempt to simulate and predict accurately the course of simple chemical reactions using multi-configuration Hartree-Fock theory (MC-SCF). The energy of interaction during the course of a collision can be divided into two distinct parts, the Hartree-Fock and correlation energy. The Hartree-Fock energy of interaction encompasses the electrostatic and induction interactions but can not describe the dynamical correlation of the electrons. Calculation of the correlation energy is essential but the difficulty of calculation has been the major obstacle in the way of obtaining useful surfaces. However, recent advances have shown that only the correlation energy contribution to the binding energy is needed to obtain energy interaction surfaces congruent with the true curves. New techniques have already worked for small systems. This study will attempt to apply and extend these techniques to a particularly important molecular system.

The specific problem in chemical dynamics which is to be treated in this work is related to the photolysis of ozone. Adiabatic potential energy surfaces for $O + O_2$ interaction will be calculated using the MC-SCF techniques. With these calculations it is hoped to determine whether there are barriers to chemical reaction and to make meaningful state correlation diagrams.

Methods and knowledge developed here should be applicable to other chemical systems.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

A. 10. Exploratory Research

Project Title: USE OF COMPTON SCATTERING FOR THE INVESTIGATION OF THE MOMENTUM AND SPACE DISTRIBUTIONS OF THE FREE AND BOUND ELECTRONS IN SOLIDS AND LIQUIDS

Principal Investigators: Professor R. Fox and Dr. J. Felsteiner

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. R. D. Deslattes

NBS Institute or Center and Division: Institute for Basic Standards
Optical Physics Division

Summary Description and Project Goals

Proposed investigation will employ relatively energetic γ source to validate certain desirable simplifying assumption regarding analysis of Compton spectra.

Results and Implications to Date

From the energy distribution of the scattered gamma rays the momentum and space distributions of the electrons of the scatterer were obtained. The scattered gamma rays were analyzed by a high resolution germanium detector.

Attention was given to separating clearly the contributions of the free and bound electrons. In particular, the free momentum distributions were studied to obtain the magnitude of the expected discontinuity at the Fermi momentum and the shape of the high momentum tail. In addition, the bound electron momentum distributions made it possible to reveal the modification of the atomic wave functions in the solid and liquid states.

The use of Compton scattering to study independent electron momenta requires the condition that neighboring electrons do not influence the scattering. It is difficult to formulate a rigorous definition of this theoretically. A minimal condition however would appear to be that the interelectron spacing be much greater than the dimension of the photon wave packet or wavelength. In the usual work the $\text{MoK}\alpha$ X-rays used do not satisfy this condition.

The only clean method with no theoretical objections that we know of for studying the individual electron momenta appears to be the present technique using high energy nuclear gamma rays. The only other method that is now being used by many research groups is positron annihilation. This method however has the theoretical complication that the incident positron polarizes the electron distribution to a density an order of magnitude greater than normal¹.

In the present investigation high energy gamma rays ($\gtrsim 60$ keV) were used. A 60 keV gamma has a wavelength one fourth that of $\text{MoK}\alpha$ X-rays. Higher energy gammas have correspondingly shorter wavelengths.

The fact that the shape of the electron momentum distribution that is obtained by positron annihilation is completely different from that obtained by $\text{MoK}\alpha$ Compton scattering emphasizes the importance of this work.

References:

1. S. Kahana et al., Phys. Rev. 117, 123 (1960); Phys. Rev. 129, 1622 (1963); Phys. Rev. 139, A213 (1965).

List of Publications that Resulted from the Project

1. "The Electron Momentum Density in Aluminum", J. Felsteiner, R. Fox and S. Kahane, Solid State Communications, Vol. 9, pp. 61-63, 1971. Pergamon Press. Printed in Great Britain.
2. "Compton Profile Anisotropy in Graphite", J. Felsteiner, R. Fox and S. Kahane, Phys. Letters, Vol. 33A, No. 7, Dec. 1970, pp. 442-443.
3. "Electron Momentum Distribution in Polycrystalline Iron", J. Felsteiner, R. Fox and S. Kahane, Solid State Communications, Vol. 9, pp. 457-459, 1971. Pergamon Press. Printed in Great Britain.
4. "Structure Factors and Compton Profile for LiH Calculated From Self-consistent Local-orbital Wave Functions", J. Felsteiner, R. Fox and S. Kahane, accepted to J.Phys. C: Solid State Physics, 4, L163 (1971).

A. 10. Exploratory Research

Project Title: COMPUTATIONAL TECHNIQUES AND NUMBER THEORY

Principal Investigator: Dr. Aviezri Fraenkel

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. Morris Newman

NBS Institute or Center and Division: Institute for Basic Standards
Applied Mathematics Division

Summary Description of Project Goals

The aim of this project is to attack and solve problems in Number Theory and related fields by means of computational techniques and to use number theoretical methods for extend-high-speed computational techniques. The major effort will be spent on problems which a computation appears to have a good chance of advancing the present state of the theory; i.e., improving known theorems, proving or disproving conjectures, or numerical explorations leading towards new conjectures. Primary emphasis will be placed on the development of high-speed computational techniques.

Results and Implications to Date

An algorithm for computing the exact solutions of linear equations with rational coefficients, and its computer implementation has been developed and described in a publication. The publication contains the complete listing of a FORTRAN program developed for carrying out this algorithm. The basic idea of the algorithm is to convert the original system of equations into a system of congruences modulo various primes p_i , and combining the solutions by a procedure suggested by the Chinese Remainder Theorem. This process is continued until the sequence of solutions modulo $p_1 p_2 \dots p_k$, $k=1, 2, \dots$ converges to the true solution. The major part of the computation is performed in single precision.

List of Publications that Resulted from the Project

1. A. S. Fraenkel and D. Loewenthal, "Exact Solutions of Linear Equations with Rational Coefficients", Journal of Research of the National Bureau of Standards, 75B, p 67 (1971).

Project Title: SOLID ASYMMETRIC STATIONARY PHASES FOR THE PREPARATIVE SEPARATION OF OPTICAL ISOMERS

Principal Investigator: Professor E. Gil-Av

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. R. Schaffer

NBS Institute or Center and Division: Institute for Materials Research
Analytical Chemistry Division

Summary Description of Project Goals

Starting from the success in producing asymmetric phases for use in gas chromatography for separating heat-stable derivatives of enantiomorphous α -amino acids, the investigator seeks to extend that approach to high pressure liquid chromatography. The ultimate objective is to provide an effective means for the resolution of the non-derivatized enantiomers, which is much to be desired and which should be feasible under the far milder conditions of liquid chromatography.

Results and Implications to Date

The principal investigator has supplied this note on the status of this recently activated grant.

"In recent years it has been demonstrated that enantiomers can be separated on optically active stationary phases by gas liquid chromatography. More particularly, it has been shown¹⁻⁴ that compounds containing an amine group attached to an asymmetric carbon can be resolved in the form of N-acyl derivatives by solvents which have a structure such as to permit hydrogen bonding between at least two points of the two molecular species involved in the immediate vicinity of the asymmetric centers.

"This new approach to the separation of optical isomers has been developed as an analytical tool especially for the natural amino acids. Problems to which this new method have been applied include the racemization of α -amino acids⁵, the conservation of configuration in the solid state synthesis of peptides⁶, the configuration of amino acids in bacterial cell walls⁷, and the evidence for life in meteorites and precambrian sediments⁸.

"A small scale preparative resolution (on mg quantities) has been successfully carried out in one case³. It is the purpose of the present project to develop procedures which would permit to separate pure enantiomers in gram quantities or even on a larger scale, using the experience accumulated in our previous work on the selective interaction of asymmetric solutes and solvents.

"Though recently large diameter columns have been introduced in gas liquid chromatography, it would be far more convenient and practical if phases were available to carry out the preparative separation of enantiomers by liquid chromatography.

"It is the main purpose of the present project to achieve this objective by the synthesis and study of appropriate asymmetric solid phases. It is felt that a successful solution will be of considerable significance in many areas of chemical and biochemical research. Such new methods of separation would further be of interest for the preparation of pure standard materials and might possibly also have industrial potential.

"The experimental part of the project involves two aspects: the synthesis of suitable asymmetric solids, and test of their ability to resolve solutes.

"After activation of the Grant in August, 1970, we have concentrated first on the assembling of the testing equipment. This consists of a high speed, high pressure liquid chromatograph, the main parts of which are a high pressure (350 atm.) feed pump linked to a damping system; a sample introduction valve; a column and a microadsorption cell. Preliminary experiments have shown that the sensitivity of the detector is satisfactory for our purpose.

"As far as the stationary phases are concerned, we started with the preparation of polystyrenes grafted with amino acid or peptide derivatives according to Merrifield⁹. This seemed to provide a good way to transfer the experience accumulated in our laboratory on resolution through amino acid derivatives by GC to the problem of finding similar selectivity in solid-liquid systems.

"The first polystyrene derivative prepared was a N-t-butoxy-carbonyl-L-leucine ester grafted on a cross linked (2%-vinylbenzene) polystyrene. The polymer was loaded with the amino acid moiety to an extent of 0.6 milli-equivalent/g. In future we shall prepare additional polymeric derivatives of this type, and study the effect of structural features on resolution. Features to be varied include: amount of cross linking, number of grafted amino acids per unit weight, nature of the amino acid or peptide derivative linked to the polymer and of the group through which linkage to the polymer backbone is effected.

"Testing of the phase has not yet been carried out, as we have had some trouble with the thermistors serving as sensors in the microadsorption cell and are waiting for spare parts to be flown in. Incidentally, after having had this mishap, we have decided to build in future our own adsorption cells, and our workshop has already completed the stainless steel frames for two such units.

"In the meantime, we have, however, tested some particularly striking reports on successful separations of enantiomers on solid asymmetric natural solids by classical column chromatography, as described by Krebs et al. (see Figure). As can be seen on the attached graph, we obtained very good separation, thus confirming the data of the authors. Out of approximately 450 mg of a racemic mixture of 3-bromocamphor-8-sulfonic acid, 50-60 mg of each of the pure antipodes could be separated. This result is very encouraging and confirms us in our belief in the potential of the approach on which this project is based."

References

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The NBS monitor has made the following recent comment:

A part of the basic research, required to reach the objectives of the grant supported by NBS, has just appeared in the publication listed below. In that work, the resolution factors obtained using the named stationary phase are the highest yet reported for resolutions of α -aminoacid derivatives on asymmetric phases.

List of Publications that Resulted from the Project

B. Feibush "Interaction between Asymmetric Solutes and Solvents. N-Lauroyl-L-valyl-t-butylamide as Stationary Phase in Gas Liquid Partition Chromatography" Chemical Communications, 544 (1971).

Project Title: ELEMENTARY PARTICLE INTERACTIONS

Principal Investigator: Dr. David Horn

Institution: Tel Aviv University

NBS Monitor: Dr. Sydney Meshkov

NBS Institute or Center and Division: Institute for Basic Standards
Center for Radiation Research

Summary Description of Project Goals

This project concerns itself with understanding the structure and interactions of subnuclear matter. The methods used complement the work of the National Bureau of Standards high energy group in its effort to understand and systematize the large amount of high energy reaction data which is currently being produced.

Results and Implications to Date

The sponsored research has treated two different areas of reaction theory. The first deals with two-body reactions and the important problem of producing a systematic description of the cause of the dips in angular distributions. The second considers one of the most important current questions in high energy physics, namely the description of processes in which many final state particles are produced. Dr. Horn and coworkers have developed interesting methods for describing such systems and have compared their results with experiment and with the parton picture.

List of Publications that Resulted from the Project

1. "Many Particle Phenomena", Dr. D. Horn, (Invited Lecture to be published in the Proceedings of the International Conference on Duality and Symmetry in Hadron Physics, Tel-Aviv, 1971).
2. "Dual Approach to Regge Dips", Y. Gell, D. Horn, M. Jacob and J. Weyers, Nuclear Physics, B 33, 379-396, 1971.
3. "Study of $NN \rightarrow \Delta N$ and its Line Reversed Reaction", G. Alexander, A. Fridman and E. Gotsman, (Paper submitted to the Amsterdam Conference on Particle Physics, 1971).
4. "Many Particle Production", D. Horn (To appear in Physics Reports.).
5. "Multiperipheral and Polyperipheral Approaches to Pionization", M. Bishari, D. Horn, and S. Nussinov, Nuclear Phys. B36, p 109-120 (1972).

A.10. Exploratory Research

Project Title: STRUCTURE, SYMMETRIES AND INTERACTIONS OF SUB-NUCLEAR MATTER

Principal Investigator: Professor H. J. Lipkin and Professor H. Harari

Institution: The Weizmann Institute of Science

NBS Monitor: Dr. S. Meshkov

NBS Institute or Center and Division: Institute for Basic Standards
Center for Radiation Research

Summary Description of Project Goals

This project concerns itself with understanding the structure and interactions of sub-nuclear matter and of its interaction with electromagnetic radiation. The methods used complement the work of the NBS high energy group in its effort to classify and systematize the large amount of spectroscopic and reaction data which is currently being produced. Owing to the fact that this project was only very recently established and in place of a section on results an extract is given from the project proposal as written by the principal investigators.

"The plans for the future include continued investigations of the above topics. Some particular lines of investigation are listed below.

I. Duality.

- A. An attempt to obtain a better understanding of the separation of an amplitude into resonances and background. The nature of the non-resonant background and its relation to the Pomeranchuk singularity.
- B. Applications to the calculation of low energy parameters.
- C. The relation to duality ideas of Regge cuts and the various types of absorption models.
- D. A search for an algebraic formulation of the duality hypothesis which could lead to a meaningful way of breaking duality.
- E. Further investigation of the difficulty arising in baryon-antibaryon scattering.
- F. A search for a quark-quark interaction which exhibits the required duality features on the hadronic level while retaining a simple fundamental force on the quark level and giving rules for the use of duality diagrams.
- G. Application of n-point Veneziano functions to mass extrapolation procedures with application to extending current algebra predictions.
- H. Implications of duality for electromagnetic and weak processes.

II. Electron Scattering.

- A. Studying the relation between the diffractive Pomeron dominance model for inelastic electron scattering and the results of current algebra.
- B. The application of this model to specific final states in elastic electron and neutrino reactions.
- C. Study of the relation between the quark version of the parton model and the duality diagrams.

III. High Energy Phenomenology, Symmetries and Quarks.

- A. Continued analyses of new experimental data and suggestions of new predictions.
- B. Application of the formulation developed for proper relativistic treatment of spin in the quark model to experimental predictions and analyses of experimental data for decay correlations."

Results and Implications to Date

This being a recently funded project, results could not possibly have been expected at this time.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

A.10. Exploratory Research

Project Title: NMR STUDY OF THE ELECTRONIC STRUCTURE OF LIQUID METALS

Principal Investigator: Dr. David Zamir

Institution: Soreq Nuclear Research Center

NBS Monitor: Dr. L. H. Bennett

NBS Institute or Center and Division: Institute for Materials Research
Metallurgy Division

Summary Description of Project Goals

The question of how much the electronic structure of a metal changes on melting is still the subject of much debate. On melting, two effects take place: (1) the metal expands and (2) order is lost. Although the influence of expansion can be readily calculated, the effect of disorder is not clear. Nowadays, it is fashionable to picture liquid metals as "random close-packed", so that in the liquid, not only long-range order is lost, but short-range order is not preserved either.

This loss of order brings about an increase in electrical resistivity and a decrease in thermal conductivity by a factor of about 2, so that the mean free path of the conduction electrons in the liquid metal is about half that in the solid. Another effect brought about by disorder is isotropy of the electronic behavior. This isotropy causes the "free-electron like" behavior suggested by the Hall effect and optical measurements.

The transport properties mentioned above are strongly dependent on order, but they are not sensitive tools for probing changes in electronic properties such as the density of states or wave-function behavior of the conduction electrons. In contrast, nuclear magnetic resonance (NMR) properties in metals like Knight shift and spin-lattice relaxation, depend explicitly on the electronic properties.

Results and Implications to Date

Dr. Zamir describes the work carried out under this recently funded program as follows:

"Using pulsed NMR methods we examined the electronic structure and properties of copper metal, in the solid and the liquid phases, up to $1300^{\circ}\text{C}^{(1a,b)}$. The results obtained may be explained by a strong volume dependence of the electronic structure, which is brought about by s-d hybridization. It is shown that the electronic structure in the liquid state is a smooth extrapolation from the solid. Thus it is concluded that loss of order upon melting has no effect upon the electronic structure.

We intend to study the effect of melting on Ag. The electronic structure of Ag is, in general, similar to that of copper, but the degree of s-d hybridization is different. This fact will enable us to check our model of the effect of volume and melting on the electronic structure of metals as applied to copper. Moreover, Ag has no nuclear quadrupole moment, which will enable us to eliminate effects that exist in copper and which may have some bearing on certain anomalies in our results. Ag has a low magnetic moment. The NMR experiments must be carried out at high magnetic field strength - we

intend to use our superconducting magnet for this purpose.

The question of the effect of order on physical properties is a highly important one and at the present time much significant scientific activity is being devoted to it. It appears that there are properties which are strongly influenced by the destruction of order, such as transport properties - electrical and thermal conductivity - ; while there are properties which are not sensitive to destruction of order.

This is a developing field in the science of materials, from which important and useful results are likely to be obtained."

List of Publications that Resulted from the Project

1. "NMR Study of Self-diffusion and the Electronic Structure of Metallic Copper in the Solid and Liquid States", U. El-Hanany and D. Zamir, Phys. Rev. 183, 809 (1969)
2. "Temperature Dependence of Electronic Structure of Solid and Liquid Copper - An NMR Study", U. El-Hanany and D. Zamir, Phys. Rev. 5B, 30 (1972).

B.1. BIOMATERIALS

Project Title: PREPARATION AND CHARACTERIZATION OF MICROCRYSTALLINE HYDROXYAPATITE

Principal Investigator: Dr. Yoram Avnimelech

Institution: Technion Research and Development Foundation, Ltd.

NBS Monitor: Dr. Walter E. Brown

NBS Institute or Center and Division: Institute for Materials Research
Polymers Division

Summary Description of Project Goals

This project will involve the preparation and characterization of microcrystalline hydroxyapatite for use as a Standard Reference Material. The purified and certified standard is important to biomedical research and will have broad applications in the agricultural, industrial and scientific communities, particularly since the material that is now available commercially is of low quality and is poorly characterized. In addition to purity determinations based on (1) chemical analysis for calcium, phosphorus and water, and (2) petrographic and infrared studies, other areas that will be investigated to help characterize the material include, solubility measurement, X-ray diffraction, gas adsorption and radiochemical exchange studies.

Results and Implications to Date

Hydroxy-apatite (HA) is a prototype of calcium phosphate crystalites common in bones, fertilizers and many industrial processes. However, at present no pure product of HA is available and the methods for the preparation of such a product are not clear.

During the first year of the project a sample was produced and analysed in the Technion's laboratories as well as at NBS. Some defects were found and the means to overcome them were discussed. At present a new batch, hopefully free of those defects, is being produced.

Among the by-products of this project are some studies on the mechanism of calcium phosphate precipitation, studies that are being prepared for publication.

In addition, the need for a good set-up for analysis, controlled by the NBS staff, has helped us to establish the equipment and personnel, both helpful for other projects.

List of Publications that Resulted from the Project

None

B.4. INORGANIC MATERIALS

Project Title: INVESTIGATION AND DEVELOPMENT OF ANALYTICAL METHODS FOR THE ESTIMATION OF TRACE IMPURITIES IN ALKALI HALIDES

Principal Investigator: Professor A. Glasner

Institution: The Hebrew University of Jerusalem

NBS Monitor: John L. Hague

NBS Institute or Center and Division: Institute for Materials Research
Office of Standard Reference Materials

Summary Description of Project Goals

The dual objectives of this project was (1) to prepare and purify several alkali halides, i.e. NaCl, KCl and KBr, for use as NBS Standard Reference Materials, and (2) to develop regently needed analytical procedures for the determination of trace impurities such as Zn, Sr, Cd, NO_3^- , NO_2^- and PO_4^- that are commonly present in these salts. Spectrophotometric methods, particularly in the U.V., were to be developed in the course of this investigation. Of immediate interest to the NBS Standard Reference Materials program was extremely pure NaCl containing known impurities at the parts per million level. A proposed certified standard of this salt was applicable to oceanographic research.

Results and Implications to Date

Although this grant has been terminated early in 1970 a paper on the determination of traces of copper in pure NaCl is in the offing; 1-10 ppm Cu can be determined spectrophotometrically in the form of the complex $(\text{Cu}(\text{CN})_3)^{2-}$. The publication of this work has been delayed, but the NBS grant will be acknowledged.

List of Publications that Resulted from the Project

1. S. Skurnik-Sarig, A. Glasner, M. Zidon and D. Weiss, "The Determination of Divalent Cationic Impurities in NaCl by Atomic Absorption, and Their Distribution in the Recrystallized Salt" Talanta, 16, 1488-1490 (1969).
2. A. Glasner, S. Skurnik-Sarig and M. Zidon, "Coprecipitation of Divalent Cations with KCl on NaCl and the Heterogeneous Nuclei Mechanism of Growth" Israel J. Chem, 7, 649-657 (1969).
3. A. Glasner, "Speculations on a New Mechanism of Crystal Growth from Aqueous Solutions" Israel J. Chem, 7, 633-648 (1969).

B.5. COMPOSITE MATERIALS

Project Title: THE REINFORCEMENT OF CONCRETE BY POLYMERS

Principal Investigator: Joseph Glucklich

Institution: Technion - Israel Institute of Technology

NBS Monitor: Thomas Reichard

NBS Institute or Center and Division: Institute for Applied Technology
Building Research Division

Summary Description of Project Goals

A new family of materials consists of ordinary concrete impregnated after hardening with a monomer which is then polymerized by radiation. In some cases the results obtained, in terms of mechanical, physical and chemical properties, are very striking. It will be the object of this investigation to study the interaction of the two component materials and to develop an understanding of the mechanism by which the polymer reinforces the concrete as a basis of a more rational design of the composite system.

This study is aimed at discovering, not a better concrete, but the mechanisms involved in the improvement of the properties of concrete when impregnated with a polymer. Its scope is therefore to discover:

- (i) The effect of the drying on the properties (the concrete must be thoroughly dried in order to impregnate).
- (ii) The effect on the properties from the filling of the voids and capillaries within the concrete.
- (iii) The effect of an adhesive bond between the aggregate and the polymer.

Results and Implications to Date

The procedures used or planned are:

- (i) Neat cement specimens of $1\frac{1}{2}$ " x $1\frac{1}{2}$ " prisms are dried out very carefully at relatively low temperatures to prevent shrinkage cracking. Specimens with visible cracks are discarded. Compressive, direct tension and flexural tests are made on unimpregnated dried specimens.
- (ii) Dried specimens are partially and fully impregnated with a monomer and activator and polymerization induced by heat. Impregnated specimens are tested in flexure, direct tension and compression.
- (iii) Bond tests are not yet under way, but the adhesive quality of the polymer to typical aggregates will be studied. In addition concretes made with these aggregates will be impregnated and the effect of the polymer on the strength will be determined.

The results obtained so far are:

- (i) Drying of the neat cement mortar increases the flexural, tensile and compressive strengths by as much as 90%. Previous work has shown similar results and has also shown that dried concrete will not creep under load.

- (ii) Success has not been achieved in partially impregnating the specimens satisfactorily. The required amount of monomer can be made to enter the specimen for partial impregnation, but when heated for polymerization the monomer becomes concentrated at certain, well defined areas. This effect may be due to the surface tension of the monomer causing it to be pulled together.

Test results indicate that the increase in direct tensile and compressive strength is a function of the amount of impregnation when compared with the dried strength. The flexural test results were inconclusive due to uneven monomer concentrations.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

B.5. Composite Materials

Project Title: SHORT AND LONG-TIME MECHANICAL CHARACTERISTICS OF FIBER REINFORCED POLYMERIC COMPOSITES UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

Principal Investigator: Dr. Ori Ishai

Institution: Technion - Israel Institute of Technology

NBS Monitor: Dr. R. S. Stromberg

NBS Institute or Center and Division: Institute for Materials Research
Polymers Division

Summary Description of Project Goals

This program is a study of the mechanical properties of glass fiber-epoxy composites. Creep tests on model composites will be carried out under simple and complex states of stress and under a variety of test modes and environmental conditions in order to evaluate the relationship between the mechanical properties of the constituent materials and the macrobehavior of the composite. It is anticipated that methods for analysis of long time mechanical performance from short time data will be evaluated.

Results and Implications to Date

The first phase of the research is concerned with the behavior of unidirectional composites loaded along the fiber orientation exposed to combined heat and humidity. Preliminary findings indicate a correlation between water absorption and longitudinal strength drop of the composite material. On the other hand, short-time loading history below 40% of ultimate does not affect longitudinal strength significantly.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

B.7. BUILDING TECHNOLOGY

B.7. Building Technology

Project Title: NEW DEVELOPMENTS, DIRECTIONS AND INNOVATIONS IN BUILDINGS AND BUILDING RESEARCH IN ISRAEL

Principal Investigator: A. Alweyl

Institution: The Standards Institution of Israel

NBS Monitor: P. R. Achenbach

NBS Institute or Center and Division: Institute for Applied Technology
Building Research Division

Summary Description of Project Goals

A factual exposition and up-to-date technical and economical evaluation of Israeli experience and research is to be given for building activity. The applicability of improvements and innovations of the construction methods in Israel to the building industry in the U.S.A. will be considered.

Results and Implications to Date

The following descriptive accounts have been completed to date:

1. Development of building methods in Israel
2. Technical description of various building systems, including description of elements, reinforcements, joint details etc. The following methods have so far been covered by the description:
 - A. Partial prefabrication in a permanent factory. Under this method the vertical elements - walls and partitions - are of precast reinforced concrete, whereas the floor slabs are cast in situ. Also stairway flights, roof parapets and blocks for the plumbing system are prefabricated.
 - B. "Complete" prefabrication in a permanent factory. The structural elements are transverse load-bearing walls, composed of R. C. prefabricated elements of room height, and prefabricated floor slab elements and external walls.
 - C. "Complete" prefabrication, according to a system developed in Israel, with "dry" joints between elements involving a minimum of concrete castings on the building site.
 - D. Building with large prefabricates produced in temporary site factories (three methods).
 - E. Building with prefabricated solid slabs, made of light cellular concrete.

Under the same heading a description will be given of some additional methods developed in Israel.

3. Comparative analysis of labor input under different building methods

In this account the results will be presented of time studies carried out at typical prefabrication plants as well as on sites where buildings have been erected with elements produced at such plants. The purpose of the studies was to determine the labor inputs required for producing and erecting the prefabricates, determined according to the category of labor (skilled and unskilled) and the kinds of the

different prefabricates. The results are also shown as amounts of labor per sq. m. of completed building.

On the strength of these detailed time studies carried out under both industrialized and conventional building methods, the relevant labor inputs will be compared on a uniform basis. In this comparison the differences due to variations in the working conditions met in the different time studies will be eliminated.

This account, too, is under preparation. Some additional time studies will be carried out, in order to complete the data needed for arriving at definite conclusions.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

B. 7. Building Technology

Project Title: PREDICTION OF THE THERMAL BEHAVIOUR OF FULL SCALE BUILDING

Principal Investigator: Dr. Baruch Givoni

Institution: Technion Research and Development Foundation Ltd.

NBS Monitor: Dr. Tamami Kusuda

NBS Institute or Center and Division: Institute for Applied Technology
Building Research Division

Summary Description of Project Goals

To compare and validate several mathematical methods for the prediction of the thermal behaviour of buildings, i.e., the pattern of their indoor air temperatures as a function of their design, their construction and of the variations in the outdoor climatic conditions. The Response Factor according to the ASHRAE procedure and the total thermal time constant methods, will receive particular analysis.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

B. 7. Building Technology

Project Title: WATER CONSERVATION MEASURES IN PLUMBING

Principal Investigator: Professor H. Ilberg

Institution: The Standards Institution of Israel

NBS Monitor: R. S. Wily

NBS Institute or Center and Division: Institute for Applied Technology
Building Research Division

Summary Description of Project Goals

The aim of this project is to determine performance of sanitary plumbing equipment or systems designed to reduce water consumption through measures such as high-efficiency sanitary fixtures and flow regulating devices.

It is intended also to carry out observations and tests on recirculating sanitary waste-disposal systems and on the "Vacuum Sewerage System" in order to ascertain whether efficient oxidation of organic waste products is feasible with small consumption of water.

Results and Implications to Date

Professor H. Ilberg, the Principal Investigator, has sent additional explanatory notes which read in part:

"In many countries of the world there exists a shortage of water due to the rapid development of science and technology. Even countries like the Netherlands, Great Britain and Switzerland where ample resources of water by nature are available, a shortage of water is felt and measures are taken to reduce the consumption of water by saving or searching for new resources of water supply. Shortage of water is especially felt in developing countries like Israel. Since Israel has very limited resources of water and big desalination projects are for the time being not available, ways for cutting the present water consumption must be sought.

The Research Project granted to the Standards Institution of Israel under Public Law 480 administered by the National Bureau of Standards has been initiated and first results in saving water are already available. The Research Project comprises the following elements:

Flushing Appliances,

Water Closet Bowls,

Flow and Pressure Regulating Devices and Controls,

Vacuum Sewerage,

Recirculating Devices in Sanitary Waste Disposal Systems.

According to the project program, flushing appliances and water closet bowls are to be investigated in the first year with the purpose of saving water."

Under the project test procedures for water closet bowls were evaluated. All the tests so far devised show much scatter so that large sample tests are needed for achievement of valid conclusions. The actual hydrodynamic flow in the bowls is complex. The effects of various shape, and flow-rate parameters were therefore empirically studied. The conclusion

reached is that the quantity of water needed for flushing can eventually be reduced to as little as 5 to 6 liters.

List of Publications that Resulted from the Project

1. "Water Conservation Measures in Plumbing", Prof. H. Ilberg, Ing. I. Silberstein and Ing. E. Winter, The Standards Institution of Israel, Report No. 32, July 1971.

Project Title: IMPROVEMENT OF THE STRENGTH OF BONDED JOINTS BY MECHANICAL SURFACE
ACTIVATION OF THE ADHERENDS

Principal Investigator: Ch. H. Lerchenthal

Institution: Technion - Israel Institute of Technology

NBS Monitor: Arthur Hockman

NBS Institute or Center and Division: Institute for Applied Technology
Building Research Division

Summary Description of Project Goals

Vigorous abrasion of the adherends is the usual method used to improve the strength of bonded joints. However, the free valency sites thus created are quickly inactivated by O_3 , O_2 , H_2O , N_2 and CO_2 . It is proposed to activate the surfaces mechanically in the presence of suitable reactive adhesives, with a view to making newly created reactive sites immediately available for strong adhesive bonds. Apart from mechanical testing of the adhesive strength of the bonds thus obtained, the degree of chemical activation will be measured directly with the aid of suitable tracer elements such as $^{18}O_2$.

Results and Implications to Date

This project was initiated in November 1970. No results are yet available.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

B.7. Building Technology

Project Title: DEVELOPMENT OF TENSILE STRENGTH, TENSILE STRAIN AND STRESS IN FRESH CONCRETE EXPOSED TO HIGH EVAPORATION

Principal Investigator: R. Shalon, D. Ravina, Ch. Jaegermann

Institution: Technion - Israel Institute of Technology

NBS Monitor: T. Reichard

NBS Institute or Center and Division: Institute for Applied Technology
Building Research Division

Summary Description of Project Goals

Previous studies of the plastic shrinkage of concrete showed that the paramount influence on the relation between the tensile stress and tensile strength on plastic cracking was caused by evaporation of water from the fresh concrete. Studies of length change measurements, rheological properties, tensile stress, tensile strength, and rate of evaporation of varied mixes exposed to different climatic conditions will be conducted for a period of ten hours after casting. It is hoped that the findings will lead to improved recommendations for concrete design in hot dry weather.

Results and Implications to Date

This grant was established only in October 1970. The instrumentation has been planned, set up and undergone preliminary tests in order to determine the accuracy and reproducibility of results. A report (see below) has been written entitled: "Tensile Stress and Strength of Fresh Mortar Subjected to Evaporation". Its abstract reads as follows:

"Since the development of tensile stress and strength in fresh mortar and concrete cast in and exposed to hot-dry climate is the decisive factor in plastic shrinkage cracking, an investigation was carried out with a view to studying the effect of the individual parameters on early stress and strength. The paper presents experimental data obtained so far, on stress and strength in fresh mortars cast under and exposed to various climatic conditions (temperature 20° and 30°C; relative humidity 45% and 35%; wind velocity 0, 9 and 20 km/hr). Other variables were: type of cement (I and V); cement content (550 and 365 kg/cu.m.) and consistency (semi-plastique and plastique)."

List of Publications that Resulted from the Project

1. "Tensile Stress and Strength of Fresh Mortar Subjected to Evaporation", a manuscript covering preliminary results prepared by Prof. R. Shalon and Dr. D. Ravina. This paper was presented at the Symposium organized by the International Union of Testing and Research Laboratories for Materials and Structures (RILEM), held from Aug. 2-5, 1971.

Project Title: ACCELERATED TEST METHOD FOR PREDICTING THE STRENGTH OF CONCRETE

Principal Investigator: M. Tenny, S. Avudi, M. Sherban

Institution: The Standards Institution of Israel

NBS Monitor: Howard T. Arni

NBS Institute or Center and Division: Institute for Applied Technology
Building Research Division

Summary Description of Project Goals

The aim of this recently terminated project was to develop a test procedure for predicting the 28-days strength of concrete by testing samples one day after casting. The developed procedure should be applicable for control tests in field laboratories.

The outline of the work was: I.) To carry out the Mandatory Test Procedures in accordance with the Cooperative Testing Program of ASTM Committee C-9. II.) In parallel to test cube specimens in accordance with ASTM methods mentioned above. III.) To prove an additional accelerated method as proposed by the Standards Institution of Israel.

Results and Implications to Date

A report has been submitted by M. Tenny, S. Avudi and M. Sherban on the "Accelerated Test Method for Predicting the Strength of Concrete".

In this report are given the results of testing all the concrete cylinders required by the Mandatory Test Procedures A, B, C. In addition, these procedures included parallel tests on 12 cm. cubes which were performed to the Standards Institute of Israel specifications for testing concrete. The results of testing the cubes will be given later.

In addition to the three mandatory procedures, two more accelerated methods were also evaluated. One marked "F1" and the second marked "D1". Both procedures are modifications of the optional procedures "F" and "D" as suggested by ASTM Subcommittee II-i of Committee C-9. In procedure "F1" the specimens tested were cylinders and cubes while in procedure "D1" only cubes were tested.

The report contains the results obtained from testing cylinder specimens cured in accordance with the accelerated methods. In addition, the report contains the results of 28-day and of 364-day tests performed on standard cured companion specimens.

The Field Control Tests suggested by this Institution are now in progress.

1. Testing Program

The various accelerated methods were applied on three groups of concrete of different composition. Concrete specimens from each unit were cast and tested

- (1) after applying the various methods for obtaining accelerated strength
- (2) after standard curing.

Group I. The compositions of the different concrete mixes (e.g., type of cement, cement content, admixtures, consistency etc.) were in accordance with the Cooperative Testing Program. Two series of concrete mixes were prepared: one with ordinary Portland cement (ASTM Type I) and the other with high early strength cement (ASTM Type III). The number of

mixes were 24. From each mix 6"x12" cylinders and 12 cm cubes were cast for test. The total number of specimens tested in this group was 752.

Group II. The compositions of the different concrete mixes in this group were proposed by the S.I.I. Taking into account local practice, four series of concrete mixes were prepared. In these series two brands of cement of Type I, one brand of cement of Type III and one brand of cement of Type V (sulfate resistant) were used. In Series No. 3 and No. 6 coarse aggregates from two different quarries were used (dolomitic & calcareous). All mixes of this group were prepared without admixtures except that to the mixes of series No. 3 a plasticizer was added. In total, 84 concrete mixes were prepared from which 2100 cubes of 12 cm were cast.

Group III. As suggested by the S.I.I., the specimens to be tested will be prepared from mixes used in casting concrete at various construction sites in Tel-Aviv area. The compositions of the concrete test specimens will therefore be unknown. The procedure of accelerating the strength of the concrete, found in the tests of Group I and Group II as most effective in assessing the potential strength of the concrete, will be applied to the specimens of this Group.

2. Description of the Accelerated Tests Procedures.

Five different curing procedures of accelerating the strength of concrete were examined. Three of them were mandatory by the ASTM Cooperative Testing Program, November 1966.

- (1) Procedure A - Hot Water Method (35°C)
- (2) Procedure B - Modified Boiling Method (100°C)
- (3) Procedure C - Fixed Set Boiling Method (100°C)

These three above mentioned curing procedures were applied to all concrete mixes of Group I and Group II. Two additional curing procedures F1 and D1 were evaluated. Both of them were suggested by S.I.I. and are modifications of the Optional Test Procedures F and D of the ASTM Program.

- (4) Procedure F1 - Final Set Hot Water Method (75°C)

This curing method was also applied to all concrete mixes of Group I and Group II.

- (5) Procedure D1 - Modified Autogeneous Curing Method.

This curing method was applied to specimens prepared from different concrete mixes of Group I and Group II.

In order to examine the influence of the environmental climatic conditions on the acceleration of the concrete strength by this method, the curing containers of the same type, were stored:

- (a) in an air-conditioned room at $22 \pm 3^\circ\text{C}$
- (b) outside the laboratory
 - (i) in the sun
 - (ii) in the shadow
 - (iii) in a refrigerator at -2°C .

2.1 The Curing Procedures.

Details of the curing procedures are given in the Report as follows: -

- (1) procedure A - hot water method (35°C)
- (2) procedure B - modified boiling method (100°C)
- (3) procedure C - fixed set accelerated curing in boiling water (100°C)
- (4) procedure F1 - final set hot water method (75°C)
- (5) procedure D1 - modified autogeneous curing method.

In the Report the authors continue by describing the general work conditions, including details on

- 3.1 the preparation of materials
- 3.2 the mixing of the concrete
- 3.3 the tests of fresh concrete
- 3.4 the preparing test specimens
- 3.5 the curing tanks
- 3.6 the curing conditions
- 3.7 and the tests on the specimens.

In accordance with the Testing Program three types of Portland cement were used:

- Type I - Normal Portland Cement
- Type III - High Early Strength Portland Cement
- Type V - Sulphate Resistant Portland Cement

They were physically and chemically characterized.

The authors in this Report do not yet attempt to analyze the results of the tests, but from recent discussions with Dr. M. Tenny at S.I.I. one of the Editors (HSP) concludes that these authors have established a close correlation between the 28-day and 364-day tests. There can be no doubt that reliable conclusions on the ultimate strength of concretes can be drawn from accelerated tests. The value of such predictions is considerable for civil engineering and building technology.

List of Publications that Resulted from the Project

Accelerated Test Method for Predicting the Strength of Concrete, The Standards Institution of Israel, October 1970.

B.8. COMPUTER TECHNOLOGY

B.8. Computer Technology

Project Title: FULL TEXT RETRIEVAL, APPLICATION TO CLASSIFICATION AND OTHER USES

Principal Investigator: Dr. Aviezri S. Fraenkel

Institution: Bar-Ilan University

NBS Monitor: Dr. S. Tauber

NBS Institute or Center and Division: Center for Computer Sciences and Technology
Systems Development Division

Summary Description of Project Goals

Development and testing of computer techniques for the classification of English-language technical text, as well as for its search, based on grammatical synthesis (use of all grammatical variants of terms), local frequencies, keywords in context, and human feedback.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

B.10. ELECTRONIC TECHNOLOGY

Project Title: Semiconductor Devices and Instrumentation in Nuclear Medicine

Principal Investigator: Professor Stephen S. Friedland

Institution: Tel Aviv University

NBS Monitor: Dr. J. A. Coleman

NBS Institute or Center and Division: Institute for Applied Technology
Electronic Technology Division

Summary Description of Project Goals

The aims of this project are: 1) determine the effect of the body environment on the response of semiconductor nuclear radiation detectors that are operated in-vivo. 2) optimize data presentation systems for in-vivo semiconductor detectors used in clinical and research applications. 3) characterize the response of in-vivo semiconductor detectors for the generally used isotopes such as P^{32} , Ca^{45} , I^{131} , Kr^{85} . 4) in collaboration with groups at other clinical and research facilities determine the advantage of the use of other semiconductor materials such as CdTe.

Results and Implications to Date

At this writing a number of semiconductor nuclear radiation detectors, capable of operating in vivo have been made available to the program. These include a (1) 3 m.m. diameter probe of 1 mil stainless steel wall thickness in the form of a hypodermic needle (2) a 2 m.m. diameter probe of 1 mil nickel wall thickness in the form of short hypodermic needle and (3) a 5 m.m. exposed silicon detector which has had its surface protected by paralene.

Calibration data, in preliminary form, has been obtained on each detector with the radioisotopes of P-32, I-131, Cr-51 and Ca-45. All such data is to be obtained at frequent intervals in order to determine its stability and reliability. Additional chemical forms of the source of such isotopes, such as DEP-32 are on order and additional isotopes such as S-35 are expected.

Vili Benary, formerly of Soreq, Nuclear Research Center and the San Francisco Medical Center of the University of California has joined the program on a full time basis. His background in radiation physics, engineering and medicine well qualified him for a responsible and active part in the program.

A data handling system for use in an operating theatre with the presently available detectors has been assembled from commercially available modules of electronics. Arrange-

ments are being made to examine a group of tissues removed from cases of stomach cancers before, during and after surgery to determine if a clinical diagnostic test for the detection of stomach cancer can be developed. Upon evaluation of this system a portable miniaturized battery operated data handling system will be constructed.

A number of hematology laboratories are to supply blood samples in various types of containers and systems in order to investigate the effect of blood coagulation on the surface of the detectors. Other body fluids will also be used.

List of Publications that Resulted from the Project

This project was funded only recently and no publication has yet resulted.

D.1. FLAMMABLE FABRICS

Project Title: PYROLYSIS OF CELLULOSIC FIBERS

Principal Investigator: Professor Menachem Lewin

Institution: Israel Fibers Institute

NBS Monitor: Mr. Henry Tovey

NBS Institute or Center and Division: Institute for Applied Technology
Office of Flammable Fabrics

Summary Description of Project Goals

The purpose of the project is to study the influence of the structure of cellulosic fibers in unmodified and in chemically modified states on their behavior in pyrolysis. Three cellulosic materials differing in structure will be obtained and characterized as to crystallinity, orientation, degree of polymerization, and functional groups. The effect of structural parameters upon the path and the extent of pyrolytic decomposition will be studied using differential scanning calorimetry, x-ray diffraction techniques, viscometry, gas chromatography, and chemical analysis.

Results and Implications to Date

This project was activated in 1971; results are therefore as yet unavailable.

E.1. INFORMATION EVALUATION, DOCUMENTATION, AND REFERENCE SERVICES

Project Title: TRANSLATION AND ABSTRACTION OF SCIENTIFIC DATA

Principal Investigator: Mr. Yitzhak Levi

Institution: National Science Foundation

NBS Monitor: Dr. H. J. White

NBS Institute or Center and Division: Office of Standard Reference Data

Summary Description of Project Goals

These services will include the arrangement for the translation into English, preparation of abstracts and extracts in English from original Russian and other foreign language material, and any other science information services as mutually agreed upon.

This project is coordinated by the National Science Foundation and supplements translation and abstraction of scientific data paid for out of funds allocated to NSF and in part also used for services requested by NBS.

Results and Implications to Date

The project has successfully supplied abstracting and extracting services for Russian literature on thermodynamic data. The project has been limited to this service since the total NBS demand for translations of scientific text books and data compilations far exceeds the financial resources available.

List of Publications that Resulted from the Project

Interested parties are requested to contact the project monitor.

Project Title: INTERNATIONAL SURVEY OF EDUCATIONAL FACILITIES IN THE FIELD OF CORROSION

Principal Investigator: Dr. D. Spector

Institution: International Congress on Metallic Corrosion

NBS Monitor: H. T. Yolken

NBS Institute or Center and Division: Institute for Materials Research

Summary Description of Project Goals

The purpose of this completed project was to carry out an international survey of educational facilities in the area of corrosion, specifically, to cover the maintenance of the necessary global correspondence and compilation of the data and distribution of it to members and representatives of the Permanent Council of the International Congress on Metallic Corrosion.

Information from the survey will be useful in overcoming the serious bottleneck of applying corrosion prevention measures because of lack of trained personnel.

Results and Implications to Date

The Report has been distributed throughout the world. It gives a listing of educational facilities in corrosion at all academic and technical levels in Australia, Austria, Belgium, Denmark, Finland, France, Germany, Great Britain, Holland, India, Israel, Italy, Japan, South Africa, Sweden, U.S.A., and under the United Nations.

List of Publications that Resulted from the Project

No scientific literature publication.

APPENDIX I

NBS PROGRAM STRUCTURE

A. Promoting Accurate, Meaningful and Compatible Scientific and Technical Measurements

1. Development, maintenance and improvement of standards for physical measurement
2. Calibration transfer services
3. Evaluation of the national measurement system
4. Benchwork data
5. Standard reference data
6. Standard reference materials
7. Research to improve physical measurements
8. Research to improve measurements on materials
9. Determination of data required by the measurement system
 - b. Properties of materials
10. Exploratory research

B. Promoting More Effective Use of Science and Technology

1. Materials science and technology
 - a. Metallurgical materials
 - b. Polymeric materials
 - c. Inorganic materials
 - d. Composite materials
2. Environmental pollution abatement technology
 - a. Air
 - b. Water
 - c. Noise
3. Building technology
4. Computer technology
5. Management sciences and operations analysis
6. Electronic technology
7. Cryogenic technology
8. Technology utilization analysis
9. Failure avoidance
10. Nuclear and radiation technology
11. Illumination technology

C. Promoting Strength in the Economy and Equity for Buyer and Seller in Trade

1. Voluntary engineering standards service
2. Measures of quantities important to commerce
3. Product performance
4. Testing laboratory evaluation
5. Fair packaging and labeling

D. Standards and Test Methods for Protection of the Public from Specified Hazards

1. Fire research
 - a. Fire research and safety
 - b. Flammable fabrics
2. Radiation safety
 - a. Radioactivity
 - b. X-rays and other ionizing radiation
 - c. Microwaves
 - d. Lasers
3. Product safety

E. Technical Information Services

1. Information evaluation, documentation, and reference services
2. Symposia, technical meetings, training courses
3. Research and development in information sciences
4. Consulting and advisory services
5. Metric system information services

APPENDIX II

PL 480 BACKGROUND HISTORY

The National Bureau of Standards has had an active foreign currency program under PL 480 (as amended) since 1961, in India, Israel and Pakistan. During 1970, Yugoslavia was added to the list of countries.

.... December 1969, there were no available excess foreign currency funds in Israel for F. Y. 1970, so, temporarily, all NBS/PL 480 funds in Israel were frozen. Limited allocations have since been made through the State Department and the Bureau of the Budget. With a large choice of excellent research opportunities in Israel our main concern, beginning with the latter half of F. Y. 1970, has been to make the best possible selection of collaborative research projects.

This selection process has been greatly influenced by a change in NBS policy guidelines. In F.Y. 1966 the NBS Director, Dr. A. V. Astin, had concentrated the use of PL 480 funds to projects in the fields of standard reference materials, standard reference data, and building technology. A review of this policy and its effects by the new NBS Director, Dr. L. M. Branscomb, led to a liberalization for NBS/PL 480 funds to be spent in any technical field of NBS mission responsibility. The formerly favored research fields are by no means to be excluded from additional support, however. Moreover, owing to time lag between commitment of funds and research results obtained, the current NBS/PL 480 program still shows strong concentration in the originally designated research fields.

Statistical Data for F. Y. 1970

During F.Y. 1970, the National Bureau of Standards had a PL 480 Program in four countries with projects at 28 institutions in 5 Program sub-categories. In all there were 68 active projects of which 43 projects received F. Y. 1970 funding. \$1,090,000 was obligated. Of this, \$4,500 was spent on travel by NBS staff.

The Law Itself

Public Law 480 of the 83rd Congress (Chapter 469, 2nd Session S245) was first enacted on July 10, 1954. After a number of minor amendments Public Law 89-808 of the 89th Congress (HR 14929) amended the original law in 1966. The present Law was to be known as "Food for Peace Act, 1966" but somehow the original designation PL 480 is still widely used. The following excerpts, appropriate for inclusion in this report, have been taken from the "Food for Peace Act, 1966".

"Sec. 2. The Congress hereby declares it to be the policy of the United States to expand international trade; ... to encourage economic development in the developing countries, . . . and to promote in other ways the foreign policy of the United States. . . . Title I - Sec. 103. In exercising the authorities conferred upon him by this title, the President shall -

- a) take into account efforts of friendly countries to help themselves toward a greater degree of self-reliance,

Sec. 104 . . . The President may use or enter into agreements with foreign countries

or international organizations to use the foreign currencies, . . . for . . . the following purposes:

- . . .b) For carrying out programs of United States Government agencies:
- . . . 2) finance international educational and cultural exchange activities. . .
- 3) collect, collate, translate, abstract, and disseminate scientific and technological information and conduct research and support scientific activities overseas including programs and projects of scientific cooperation between the United States and other countries. . .
- . . . 5) finance under the direction of the Librarian of Congress, in consultation with the National Science Foundation and other interested agencies,
 - (A) programs outside the books, periodicals, and other materials to determine whether they would provide information of technical or scientific significance in the United States. . .
 - (B) the registry, indexing, binding, reproduction, cataloging, abstracting, translating, and dissemination of books, periodicals, and related materials. . .
 - (C) the acquisition of such books, periodicals, and other materials and the deposit thereof in libraries and research centers in the United States specializing in the areas to which they relate:. . .
- . . .f) To promote multilateral trade. . ."
- g) For the purchase of goods or services for other friendly countries;

Provided, That-

- (1) Section 1415 of the Supplemental Appropriation Act, 1953, shall apply to currencies used for the purposes specified in subsections (a) and (b), . . .

Title IV - Sec. 404. The programs of assistance undertaken pursuant to this Act shall be directed toward attainment of the humanitarian objectives and national interest of the United States.

Sec. 407. There is hereby established an advisory committee. . .the advisory committee shall survey the general policies relating to the administration of the Act, including the manner of implementing the self-help provisions,. . .

Sec. 408. The President shall make a report to Congress not later than April 1 each year with respect to the activities carried out under this Act during the preceding calendar year. Such report shall describe the progress of each country with which agreements are in effect. . ."

The NBS/PL 480 Program

The Law challenges imaginative implementation at the same time as it offers the opportunity for international collaboration to universal benefit. In the mission area of NBS and with the available countries Dr. Lewis M. Branscomb, Director of NBS, has called for an effective program. To this end Mr. H. Steffen Peiser, as program manager, under the supervision of Dr. E.L. Brady, Associate Director for Information Programs, has received universal support, which is hereby gratefully acknowledged.

Stated NBS Policy on the NBS/PL 480 Program

Background

The United States Government acquires foreign currencies in the course of its overseas operations. The largest source of foreign currencies is from the sale of surplus farm commodities within the limits established by Title I of Public Law 480. These currencies are kept in Treasury Department accounts and are available to Government agencies to finance overseas activities.

Excess foreign currencies are the U.S. owned currencies of those countries in which the Treasury Department has found the supply to be greater than required for normal U.S. demands for the next two or three years. The Treasury Department designates foreign countries for which currency supply exceeds demands as "excess foreign currency countries".

The Congress makes a separate appropriation to NBS for the purchase of excess foreign currencies; this appropriation is supplementary to, not a substitute for, the regular Bureau appropriation. The official appropriation title is Research and Technical Services, Special Foreign Currency Program. This program is also referred to as the Foreign Currency Program or the PL-480 Program. At NBS the Program operates under the provisions of Section 104(k) of Public Law 480 ("To collect, collate, translate, abstract, and disseminate scientific and technological information and to conduct research and support scientific activities overseas including programs and projects of scientific cooperation between the United States and other countries. . . .").

Policy (NBS Policy Guide No. 1 - April 30, 1970)

The PL 480 Program provides supplementary resources that provide an appropriate means for accomplishing certain NBS objectives. Its general purpose is to aid the accomplishment of NBS goals in a manner consistent with U.S. foreign policy objectives. NBS criteria for this purpose have been listed in the Foreward. These are:

1. All projects must be of scientific or technological excellence.
2. All projects must be within the mainstream of NBS interests or contribute directly to NBS effectiveness.
3. All projects must benefit both the U.S. and the participating countries:
 - (a) NBS/PL 480 funds must not merely replace otherwise available country funds; and
 - (b) Individuals or institutions abroad must not become primarily dependent upon NBS for long term support.
4. All projects must be followed closely by NBS staff members working in related areas. Thus, one or more NBS staff should maintain a continuing direct relationship with the foreign person or group. This relationship should be strengthened by visits in either or both directions.
5. NBS involvement with a technical institution of another nation should be consistent with U.S. foreign policy. For example, relationships with sister institutions, staff exchanges, and visits should be carried on in the context of overall U.S. objectives in its relationships with the other country.

6. NBS staff travel to participating foreign countries should be exploited, when practical, by suitable additional itinerary to identify additional targets for bilateral benefit or to provide additional strength to existing relationships. Such travel should be coordinated with the PL 480 Program Manager.

Bureau Level Management

Mr. H. Steffen Peiser has been designated the NBS PL 480 Program Manager by the Director. As such he has the following responsibilities and authorities:

1. Makes final decisions on grant proposals, allocates funds, and signs PL 480 grant or contract documents.
2. Serves as the principal point of contact with:
 - a. The Director on PL 480 Program policy,
 - b. The Institutes and Centers on specific proposals and program planning,
 - c. The Budget Division on all budget related matters,
 - d. The Procurement Section on grant execution and administrative matters,
 - e. The Office of International Relations on matters of channeling communications and relations with the Department of State.
3. Authorizes all foreign travel for the PL 480 Program.

Institute Level Management

Each major organizational unit has the following responsibilities:

1. Technically evaluates proposals and determines whether the proposals meet Criteria 1, 2 and 4 of the PL 480 policy statement for support under the program.
2. Recommends proposals to the PL 480 Program Manager for support and makes priorities known to him.
3. Assures that there is continuing involvement by the designated monitor once a grant has been let.
4. Advises and assists the PL 480 Program Manager in formulating program plans and budget requests.

APPENDIX III

LIST OF PL 480 GRANTS IN ISRAEL

| Date First Authorized | Title | Principal Investigator | NBS Office, Center or Institute | NBS Monitor | Funds Committed Prior to Dec. 1971 (k\$) | Page |
|-----------------------|--|------------------------|---------------------------------|----------------|--|------|
| 4/62 | High magnetic field facility | P. Hillman | - | L. H. Bennett | 23.6 | * |
| 8/62 | Calculations in atomic spectra with special reference to rare earth spectra | Y. Shadmi | - | W. C. Martin | 143.2 | * |
| 8/62 | Lifetime and line shape measurements of spectra of rare earth ions in crystals | W. Low | - | R. P. Hudson | 138.2 | * |
| 8/62 | Excluded volume study of multi-component polyelectrolyte systems | H. Eisenberg | - | C. A. J. Hoeve | 72.6 | * |
| 8/62 | Molecular interactions in gaseous systems by means of studies of spectral line shapes and shifts | J. H. Jaffe | - | D. R. Lide | 34.5 | * |
| 8/62 | Chromotography | E. Gil-Av | - | R. E. Ferguson | 35.1 | * |
| 8/62 | Solid state polymerization | G. M. J. Schmidt | - | S. Block | 57.6 | * |
| 8/62 | Infrared studies of adsorbed molecules | M. Folman | - | R. Klein | 73.8 | * |

* Fully reported prior to FY 1970.

| Date First Authorized | Title | Principal Investigator | NBS Office, Center of Institute Monitor | Funds Committed Prior to Dec. 1971 (k\$) | Page |
|-----------------------|---|------------------------|---|--|------|
| 8/62 | Theoretical and experimental studies in the Mossbauer effect | H. J. Lipkin | - M. Danos | 15.1 | * |
| 4/63 | Infrared emissivity measurements on heated gases | U.P.Oppenheim | - A. M. Bass | 47.7 | * |
| 4/63 | Isotopic dipole moment differences | E. A. Halevi | - A.A. Maryott | 56.6 | * |
| 4/63 | Character tales of irreducible representatives of non-symmmorphic space groups | J. Zak | - A. Kahn | 21.9 | * |
| 4/63 | Studies in radioactivity and and nuclear spectroscopy | S. G. Cohen | - R. Hayward | 40.2 | * |
| 4/63 | Temperature and viscosity dependence of photo-isomerization reactions | E. Fischer | - L. Wall | 55.2 | * |
| 6/63 | Creep of lightweight concrete | J. Glucklich | - D. Watstein T.W. Reichard | 24 | * |
| 2/64 | The recording and interpretation of natural sound waves at infrasonic frequencies | A. Calo | IBS R. K. Cook | 59.6 | * |
| 4/64 | Calculation of energy levels and moments of nuclear states at low excitation | A. De-Shalit | IBS H.W. Koch | 70 | * |

* Fully reported prior to FY 1970.

| Date First Authorized | Title | Principal Investigator | NBS Office, Center or Institute | NBS Monitor | Funds Committed Prior to Dec. 1971 (k\$) | Page |
|-----------------------|--|------------------------|---------------------------------|---------------|--|------|
| 5/64 | Vacuum ultraviolet techniques for the investigation of the adsorbed state | O. Schnepp | IBS | A. Bass | 36.1 | * |
| 5/64 | NMR of rare earth nuclei in magnetic rare earth metals and oxides | W. Low | IMR | T. Farrar | 107.1 | * |
| 6/64 | X-ray absorption spectroscopy through single crystals | E. Alexander | IMR | R. Deslattes | 42.2 | * |
| 6/64 | Rare earth spectra | S. Held | IBS | B.F. Scribner | 9.5 | * |
| 5/65 | The volume of lightweight and normal weight cement mortars | J. Glucklich | IAT | E. O. Pfrang | 7.7 | * |
| 6/65 | Mechanisms of electrical breakdown in thin film dielectrics | N. Klein | IBS | F.R. Kotter | 36.8 | * |
| 9/65 | Precise x-ray and neutron diffraction studies of bond types in small organic molecules | G.M.J. Schmidt | IMR | S. Block | 111.3 | * |
| 9/65 | The determination of rate constants of the isotopic exchange between oxygen atoms and simple oxygen containing molecules | F. S. Klein | IBS | J. T. Herron | 45 | * |
| 9/65 | Computational techniques and number theory | A. S. Fraenkel | IBS | M. Newman | 21.7 | * |

* Fully reported prior to FY 1970.

| Date First Authorized | Title | Principal Investigator | NBS Office, Center or Institute | NBS Monitor | Funds Committed Prior to Dec. 1971 (k \$) | Page |
|--------------------------|--|---------------------------|---------------------------------------|----------------|---|------|
| 9/65 | Crystallographic and chemical study of the products of the thermal decomposition of alkali-metal permanganates | F. H. Herbststein | IMR | H. F. McMurdie | 55.3 | * |
| 9/65 | Trace analysis by anodic stripping voltammetry | M. Ariel | IMR | J. K. Taylor | 39.2 | * |
| 10/65 | A Mossbauer effect of superpara- magnetism | S. Shtrikman D. Treves | IMR | R. H. Kropshot | 45.4 | * |
| 10/65 | Observations, description and analysis of the spectra of neutral and singly-ionized erbium and holmium | N. Spector | IBS | W. C. Martin | 55 | * |
| 2/67 | a-c power measurements | S. Stricker | IBS | R. S. Turgel | 30.4 | * |
| 11/67 | Critical review of scaled and mathematical models for prediction of transient heat flow and indoor temperatures in buildings | B. Givoni | IAT | B. A. Peavy | 8.6 | * |
| 2/68 | Computational techniques and number theory | A. S. Fraenkel | IBS | M. Newman | 13 | * |
| 3/68 | Observations, description and analysis of the spectra of neutral and singly-ionized erbium and holmium (continuation of project dated 10/65) | N. Spector | IBS | W. C. Martin | 13 | * |

* Fully reported prior to FY 1970.

| Date First Authorized | Title | Principal Investigator | Center or Institute | NBS Monitor | Funds Committed Prior to Dec. 1971 (k\$) | Page |
|-----------------------|---|--------------------------|---------------------|------------------|--|------|
| 3/68 | International survey of educational facilities in the field of corrosion | D. Spector | IMR | H. T. Yolken | 4.5 | |
| 4/68 | Trace element analysis of SRM | S. Amiel | IMR | P. LaFleur | 30 | * |
| 4/68 | Complex stability constants | Y. Marcus A.S. Kertes | Office of SRD | H. J. White | 4 | |
| 5/68 | Calculations of Atomic spectra of the transition groups and of the rare earths | Y. Shadmi | IBS | W. C. Martin | 45 | * |
| 5/68 | The spectroscopy of two-electron atoms | C. L. Pekeris | IBS | S.A. Rossmassler | 20 | * |
| 5/68 | Development of a power measurement system for audio an accuracy of 0.1% | S. Stricker | IBS | R. S. Turgel | 45.5 | |
| 5/68 | Trace analysis anodic stripping voltammetry | M. Ariel | IMR | J. K. Taylor | 69.3 | |
| 6/68 | Determination of trace constituents in high-purity standard reference materials by spectrochemical techniques | S. Held | IMR | B.F. Scribner | 10.2 | * |
| 6/68 | Accelerated test method for predicting the strength of concrete | M. Tenny M. Serban | IAT | H. T. Arni | 43.5 | |

* Fully reported prior to FY 1970.

| Date First Authorized | Title | Principal Investigator | NBS Office, Center or Institute | NBS Monitor | Funds Committed Prior to Dec. 1971 (k \$) | Page |
|-----------------------|--|--------------------------|---------------------------------|----------------|---|------|
| 6/68 | Translation and abstraction of scientific data | Y. Levi | Office of SRD | H. L. White | 16 | |
| 7/68 | Preparation and characterization of microcrystalline hydroxyapatite | Y. Avnimelech | IMR | W. E. Brown | 27.2 | |
| 7/68 | Production and supply of metal oxide SRM by thermal decomposition of chloride salts in a spray reactor | E. Foa | IMR | J. L. Hague | 70.4 | |
| 7/68 | Mossbauer spectroscopy standards for carbon steels | Moshe Ron | IMR | M. R. Meyerson | 16.6 | |
| 8/68 | Chemical microstandards | G. Schmuckler | IMR | D. H. Freeman | 44.3 | |
| 8/68 | Analytical determination of minute quantities of rare earth | R. Reisfeld | IMR | O. Menis | 21.5 | |
| 8/68 | Investigation and development of analytical methods for the estimation of trace impurities in alkali halides | A. Glasner | IMR | J. L. Hague | 13 | |
| 2/70 | Trace element analysis of SRM's | S. Amiel | IMR | P. D. LaFleur | 75 | |
| 2/70 | Complex stability constants | Y. Marcus A.S. Kertes | IAT | H. J. White | 7 | |

* Fully reported prior to FY 1970.

| Date First Authorized | Title | Principal Investigator | NBS Office, Center or Institute | NBS Monitor | Funds Committed Prior to Dec. 1971 (k \$) | Page |
|-----------------------|---|------------------------|---------------------------------|----------------|---|------|
| 2/70 | The spectroscopy of two-electron atoms | C. L. Pekeris | Office of SRD | W. C. Martin | 42 | |
| 2/70 | Description and analysis of the spectra of neutral singly-ionized erbium and holmium | N. Spector | Office of SRD | W. C. Martin | 23 | |
| 2/70 | New developments, directions and innovations in buildings and building research in Israel | A. Alweyl | IAT | P.R. Achenbach | 12 | |
| 3/70 | Water conservation measures in plumbing | H. Ilberg | IAT | R. S. Wylly | 57 | |
| 3/70 | Development of standard reference materials for calibration of instruments in fluorescence measurements | R. Reisfeld | IMR | O. Meñis | 90 | |
| 3/70 | Chemical microstandards | G. Schmuckler | IMR | D.H. Freeman | 44.3 | |
| 3/70 | Ultra-purification of palladium cylinders used as a calibration material for magnetic susceptibility measurements | M. Schieber | IMR | G. Candela | 20 | |
| 4/70 | Study of band structure by the differential optical methods | Y. Yacoby | IMR | A. Feldman | 38 | |
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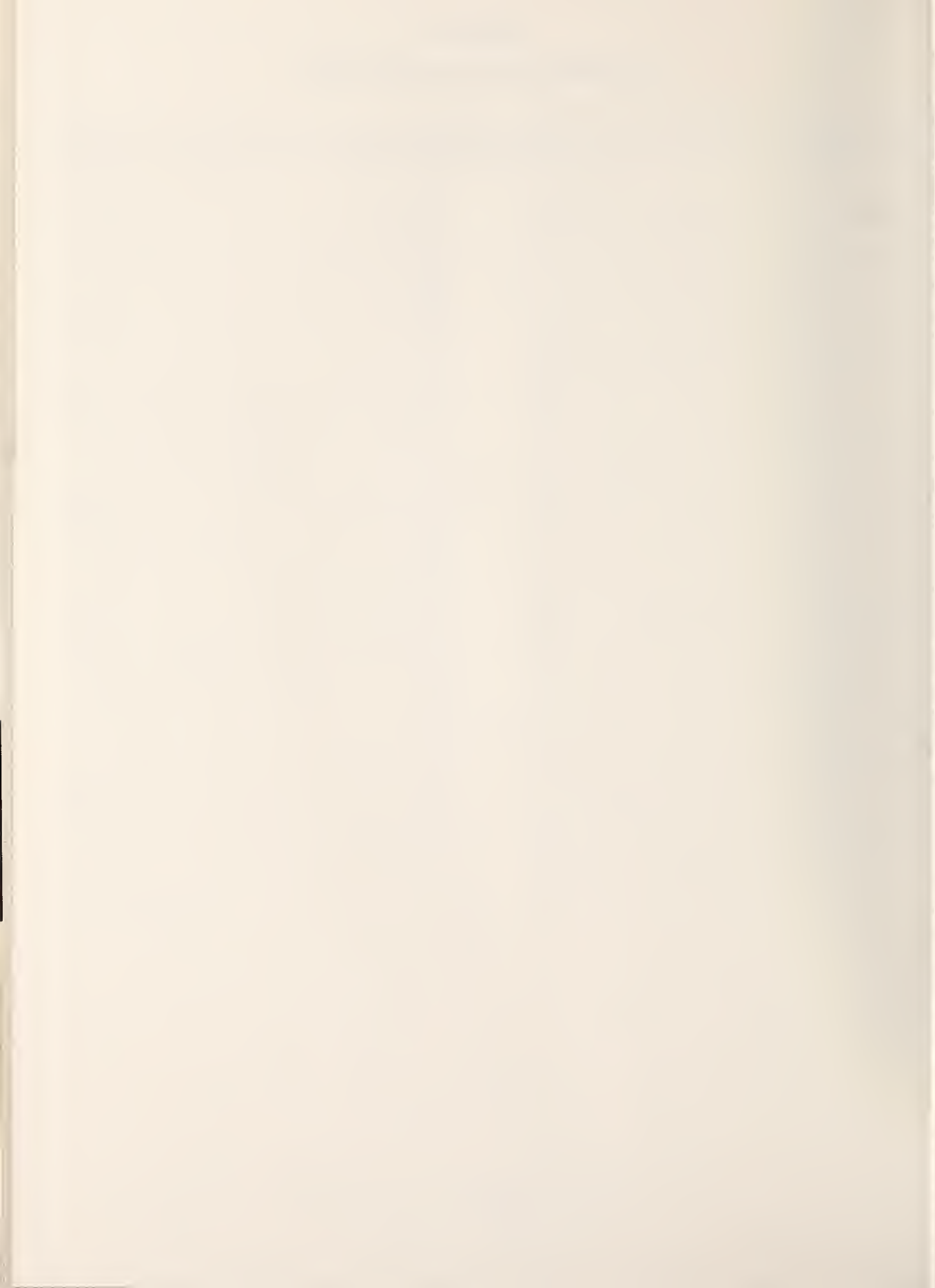
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